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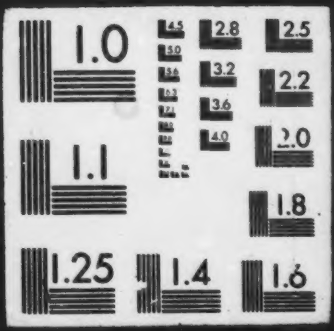
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DEVELOPMENT OF THE CATALYTIC CHAMBER PROCESS

Tyco Laboratories, Inc.

PREPARED FOR
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September 1972

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Environmental Protection Technology

Development of the Catalytic Chamber Process, Final Report

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EPA-R2-72-038

Development of the Catalytic Chamber Process, Final Report

By

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Tyco Laboratories, Inc.
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Contract No. 68-02-0008
Program Element 1A2013

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September 1972

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The results are presented of a contract period. The goal of the contract was to continue the development of the Tyco Catalytic Chamber Process for the simultaneous removal of SO_2 and NO_x from power plant flue gases. More specifically, the contract goals were as follows: (1) Modification of the existing 10 SCFM miniplant to permit integrated operation; (2) Experimentation in the integrated miniplant to determine probable design ranges of critical engineering parameters. A parametric study showing the effect of the various parameters was planned; (3) Preliminary design of a 2000 to 5000 SCFM pilot plant; (4) Evaluation of control levels of SO_2 and NO_x attainable through use of the Catalytic Chamber Process and comparison with desired levels; (5) Evaluation of the economic feasibility of the overall process and comparison with EPA standards; (6) Preliminary process control evaluations; (7) Determination of a site for the pilot plant; (8) Evaluation of the fly ash problem. The most significant results of the program were: (1) The SO_2 gas phase oxidation by NO_2 was found to proceed too slowly to permit the use of practical-sized equipment; (2) Absorption of equimolar quantities of NO and NO_2 was not to be controlled by a conventional absorption mechanism probably dependent on a gas phase interaction of the two oxides. As a result, the large equipment needed to provide long residence times makes the process appear relatively expensive for removing SO_2 and NO_x together or NO_x alone.

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ABSTRACT

The goal of this contract was to continue the development of the Tyco Catalytic Chamber Process for the simultaneous removal of SO_2 and NO_x from power plant flue gas. As originally conceived, the process involved the gas phase oxidation of SO_2 with NO_2 followed by the high temperature absorption of the nitrogen oxides in sulfuric acid. The dissolved oxides of nitrogen were recovered and oxidized in a catalytic stripper. The process produced nitric and sulfuric acids.

The results of the program conducted in a 10-SCFM miniplant were:

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1. The SO_2 gas phase oxidation by NO_2 was found to proceed too slowly to permit the use of practical-sized equipment. However, by contacting the flue gas with 2 wt % nitrosylsulfuric acid in 70% sulfuric acid in a packed bed reactor, 90% removal of SO_2 could be accomplished at 225 °F in less than 15 sec.

2. Absorption of equimolar quantities of NO and NO_2 was not found to be controlled by a conventional absorption mechanism, but is probably dependent on a gas phase interaction of the two oxides. As a result, the large equipment needed to provide long residence times makes the process appear relatively expensive for removing SO_2 and NO_x together or NO_x alone.

Table of Contents

Section Page No.

I. SUMMARY 1

II. INTRODUCTION 9
  A. Content of This Report 9
  B. Initial Process Concept 9
  C. Prior Work 10
  D. Contract Goals 11

III. ENGINEERING SUBCONTRACTOR – THE BADGER CORPORATION 13
  A. Engineering Consultation 13
  B. Optimization Program 13
  C. Pilot Plant Design 13

IV. MINIPLANT MODIFICATION AND EQUIPMENT 15
  A. Existing Equipment 15
  B. SO_2 Oxidation Reactor 15
  C. Scrubber Columns 15
  D. Stripper Columns 17
  E. Liquid Pumps 21
  F. Gas Pumps 21
  G. Instrumentation 22
  H. Gas Feed 22
  I. Miniplant Operation 24

V. REACTOR EXPERIMENTS 25
  A. Background 25
  B. Reactor Experiments: Effect of UV Radiation 25
  C. Miniplant Tests: Effect of Temperature on SO_2 Oxidation Rate 27
  D. Effect of Acid Irrigation on SO_2 Oxidation Rate 27
  E. Instrumentation Considerations 35
  F. Effect of Irrigation of Reactor with Nitrosylsulfuric Acid 38
  G. SO_2 Oxidation Reaction Mechanisms 54

VI. SCRUBBER EVALUATION 63
  A. Initial Concept 63
  B. Experimental Procedures 63

Preceding page blank

Table of Contents (Cont)

Section Page No.

C. Initial Experimentation – Parametric Study 64
D. Mathematical Analysis of Experimental Scrubber Data 67
E. Analysis of Scrubber/Stripper Data 74

VII. STRIPPER EVALUATION 81
A. Initial Concept 81
B. Laboratory Scale Stripper Tests 81
C. Miniplant Experimentation 82
D. Analysis of Stripper Mechanism 83

VIII. PROCESS CONTROL 85
A. Goals 85
B. Power Plant Operating Conditions 85
C. Instrumentation Requirements 87
D. Process Control Requirements 91

IX. ECONOMIC EVALUATION 95
A. Prior Evaluations 95
B. New Process Concept 95
C. Cost of NO_x Removal Only 101

X. CONCLUSIONS AND RECOMMENDATIONS 113
A. Conclusions 113
B. Recommendations 114

XI. ACKNOWLEDGMENTS 117

XII. REFERENCES 119

Appendices

I. PRELIMINARY ENGINEERING ANALYSIS OF THE TYCO CATALYTIC CHAMBER PROCESS BY BADGER CORPORATION I-1

II. MINIPLANT OPERATION II-1

III. DATA FROM MINIPLANT REACTOR EXPERIMENTATION III-1

IV. DATA FROM SCRUBBER/STRIPPER EXPERIMENTS IV-1

V. METAL ION INTERFERENCE IN SCRUBBER AND STRIPPER OPERATION V-1

Table of Contents (Cont.)

Appendices

Page No.

VI. CORROSION IN MINIPLANT EQUIPMENT VI-1

VII. MATHEMATICAL ANALYSIS OF SCRUBBER/STRIPPER DATA VII-1

VIII. LABORATORY STRIPPER TESTS VIII-1

IX. INSTRUMENTATION CALIBRATION IX-1

X. OXIDATION OF NO TO NO_2 FOR MINIPLANT GAS FEED X-1

List of Illustrations

Figure No. Page No.

1. Catalytic chamber process 3
2. Schematic flowsheet of miniplant 16
3. Sketch of 19-ft scrubber 18
4. Miniplant stripper column and catalyst bed support structure 19
5. Stripper column using glass pipe 20
6. Modified miniplant layout 23
7. Miniplant reactor experiments – SO_2 oxidation. Effect of water vapor in flue gas, residence time, and temperature 29
8. Configuration of miniplant reactor during initial experimentation involving liquid irrigation 31
9. Miniplant reactor experiments – SO_2 oxidation. Effect of reactor irrigation with 80% H_2SO_4 32
10. Miniplant reactor experiment – SO_2 oxidation. Effect of acid or water irrigation in packed reactor 33
11. Miniplant reactor experiment – SO_2 oxidation. Comparison of acid irrigation, wetted wall tests, and no irrigation 34
12. Miniplant reactor experiments – SO_2 oxidation. Comparison of wetted-packing reactions with and without additional unpacked residence volume 36
13. Miniplant reactor experiment – SO_2 oxidation. Evaluation of low O_2 level in flue gas 37
14. NO_2 interference calibration curve 39
15. Miniplant reactor experiment – SO_2 oxidation. Tracing of instrumentation recorder input 40
16. Miniplant reactor experiment – SO_2 oxidation. Tracing of instrumentation recorder output 41
17. Miniplant reactor experiment – SO_2 oxidation. Comparison of acid and nitrose irrigation 43
18. Miniplant reactor experiment. Effect of $HNSO_5$ concentration on SO_2 removal yield 45
19. Miniplant reactor experiment. Effect of $HNSO_5$ concentration on SO_2 removal yield 46
20. Miniplant reactor experiment. Effect of $HNSO_2$ concentration on SO_2 removal yield 47

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List of Illustrations (Cont.)

Figure No. Page No.

21. Miniplant reactor experiment. Effect of H_2SO_4 concentration on SO_2 removal yield 48

22. Miniplant reactor experiment. Effect of residence time on SO_2 removal yield 49

23. Interpretation of miniplant reactor experimentation. Tradeoff between $HNSO_2$ concentration and irrigation flow rate in achieving a specific SO_2 reaction yield 50

24. Miniplant reactor experiments. Effect of irrigation and residence time on SO_2 removal yield 51

25. Miniplant reactor experiments. Effect of countercurrent versus cocurrent reactor configurations 53

26. Scrubber/stripper parametric study and data sheet 65

27. Series stripper configuration 69

28. First order reaction rate constant K_1 as a function of NO_x inlet concentration. Data from Tyco and EPA 76

29. Second order reaction rate constant K_2 as a function of NO_x inlet concentration. Data from Tyco and EPA 77

30. Standard deviation for first order rate constant values, 85% confidence limits 78

31. Standard deviations for second order rate constant values 79

32. Graph of power plant operating parameters 88

33. Major process control requirements 92

34. Flowsheet showing the Tyco catalytic chamber process used for NO_x removal only 96

35. Proposed flowsheet for catalytic chamber process utilizing a wetted reactor for SO_2 oxidation 100

36. Extrapolation of data from Run 92 to give scrubber column height for reducing NO_x concentration from 6000 ppm to 100 ppm 102

37. Extrapolation of data from Runs 85c, 86c, 92c, 93, and 96c to give scrubber column height for reducing NO_x concentration from 2000 ppm to 100 ppm 107

38. Catalytic chamber process using a low temperature scrubber 115

List of Tables

Table No. Page No.

I. Initial Reactor Studies 26

II. Gas Phase SO_2 Oxidation with NO_2 in the Presence of UV Radiation 28

III. Degree of Conversion of SO_2 at 150°C in 80% Sulfuric Acid for Various Residence Times with Diffusion of SO_2 Being the Rate Limiting Step 60

IV. Degree of Conversion of SO_2 at 150°C in 80% Sulfuric Acid for Various Residence Time with Rate of Conversion Equal to 1/10 of the Diffusion Limited Rate 61

V. Degree of Conversion of SO_2 at 150°C in 80% Sulfuric Acid at Various Residence Times Using Modifying Assumptions Presented in Text 61

VI. Parametric Study and Supplemental Work Plan 68

VII. CO_2 Analysis of Laboratory Stripper Tests 84

VIII. Economics of NO_x Scrubbing Plant for 500-MW Power Plant Based on Tyco SO_2 Removal Process 97

IX. Economics of NO_x Scrubbing Plant for 500-MW Power Plant Based on Tyco SO_2 Removal Process 98

X. Economics of NO_x Scrubbing Plant for 500-MW Power Plant Based on Tyco SO_2 Removal Process 99

XI. Economics of SO_2/NO_2 Scrubbing Plant for 800-MW Power Plant 103

XII. Economics of SO_2/NO_x Scrubbing Plant for 800-MW Power Plant 104

XIII. Economics of SO_2/NO_x Scrubbing Plant for 800-MW Power Plant 105

XIV. Economics of SO_2/NO_x Scrubbing Plant for 800-MW Power Plant 106

XV. Economics of NO_x Scrubbing Plant for 800-MW Power Plant 108

XVI. Economics of NO_x Scrubbing Plant for 800-MW Power Plant 109

XVII. Economics of NO_x Scrubbing Plant for 800-MW Power Plant 110

XVIII. Economics of NO_x Scrubbing Plant for 800-MW Power Plant 111

I. SUMMARY

During the four and one-half year period between October 1967 and March 1972, Tyco Laboratories, Inc., has been involved in the development of the Catalytic Chamber Process for the removal of sulfur dioxide and nitrogen oxides from power plant flue gas. Under contract to the Department of Health, Education and Welfare and the Environmental Protection Agency (Contracts PH 86-68-75, CPA 70-59, and 68-02-0008), Tyco has brought the process from the conceptual stage through several major modifications to the pre-pilot stage where a reasonable decision could be made on its economic and technological viability.

The development work on the process was aimed at solving one of the major environmental problems facing our society: air pollution caused by flue gases from power stations burning fossil fuels. A typical 800 MW, coal-burning power plant produces almost 1.5 million standard ft^3/min of stack gas containing about 0.3% sulfur dioxide and 0.05% nitrogen oxides. These pollutants are equivalent to 900 tons and 100 tons of sulfuric and nitric acids (100% basis), respectively, being dumped into the atmosphere daily. Both species represent a serious hazard to man and his artifacts as well as to plant and animal life in general. The magnitude of the sulfur dioxide problem can be demonstrated by the fact that more sulfuric acid equivalent is dumped into the atmosphere from individual sources than is used for all commercial applications (and it should be remembered that sulfuric acid is the largest tonnage chemical commodity marketed today).

The need for power plant flue gas cleanup is urgent, but the very magnitude of the problem which creates this urgency is its biggest impediment. Flue gas cleanup involves the handling of enormous volumes of gas; ducts are typically 15 to 20 ft in diameter. Any process which would require reaction residence times beyond a few seconds is extremely unattractive economically because of the very high cost of large gas handling equipment. Other major obstacles to a viable process are the need for heat transfer with the flue gas and the disposal problem of the recovered pollutant. As will be seen, the original concept of the Catalytic Chamber Process avoided most of the major technological problems, while giving a relatively attractive economic outlook.

The process concept is based on the century-old Lead Chamber Process for sulfuric acid manufacture. This obsolete process made use of nitrogen dioxide to oxidize sulfur dioxide (about 13%) to sulfuric acid, which was formed in large lead chambers. The nitric oxide which

was formed during this oxidation was slowly air-oxidized back to nitrogen dioxide to permit the complete oxidation of sulfur dioxide before the gas left the lead chambers. The gas was then scrubbed with cold sulfuric acid to remove residual sulfuric acid and oxides of nitrogen. The gas was dumped to the atmosphere while the nitrated acid (nitrose) was recycled to permit continued use of the nitrogen dioxide oxidant.

Early experimentation at Tyco indicated that sufficiently rapid oxidation of sulfur dioxide in power plant flue gas (about 0.3%) could be achieved to convert the gaseous oxide to sulfuric acid in short enough residence times to permit the use of practical-sized equipment. The simultaneous reoxidation of nitric oxide to nitrogen dioxide could not be accomplished fast enough to be economically feasible, making it clear that the Lead Chamber Process could not be used directly for dilute gas cleanup. In addition, the cold scrubbing of the wet flue gas (about 7% water) caused excessive dilution of the recycle scrubbing acid, creating a need for large amounts of heat to reconcentrate the acid. Even more heat was needed to recover the oxides of nitrogen to permit the recycle of both the gasses and the scrubbing acid.

These problems were conceptually solved during subsequent experimentation by the evolution of the Catalytic Chamber Process. (See Fig. 1.) In this scheme, the dilute sulfur dioxide is oxidized to sulfuric acid with an amount of nitrogen dioxide equal to twice the stoichiometric requirement.

$$SO_2 + 2NO_2 \rightarrow SO_3 + NO + NO_2$$

Thus, half the nitrogen dioxide is converted to nitric oxide, resulting in a one to one mole ratio of nitrogen dioxide and nitric oxide which is essential for absorption in sulfuric acid:

$$NO + NO_2 + 2H_2SO_4 \rightarrow 2HNSO_5 + H_2O$$

The nitrogen oxide and sulfuric acid in the gas stream are absorbed in a high temperature scrubber. The scrubber is maintained at a temperature such that the vapor pressure of water over the effluent acid is equal to the partial pressure of water in the incoming gas (for 7% water in the gas the scrubber temperature would be about 250 °F). In this manner, the process avoids the pickup of water from the flue gas and thus avoids the need for additional heat for concentrating the acid.

The effluent nitrose from the scrubber is fed to a chamber packed with activated charcoal. Here the dissolved oxides of nitrogen are oxidized to nitrogen dioxide, which, being only very slightly soluble in sulfuric acid, bubbled out of the acid ready for recycle.

$$4HNSO_5 + 2H_2O + O_2 \xrightarrow[\text{charcoal}]{\text{activated}} 4H_2SO_4 + 4NO_2$$

This stage was shown experimentally to occur in the 250 to 300 °F temperature range, again avoiding the need for heat.

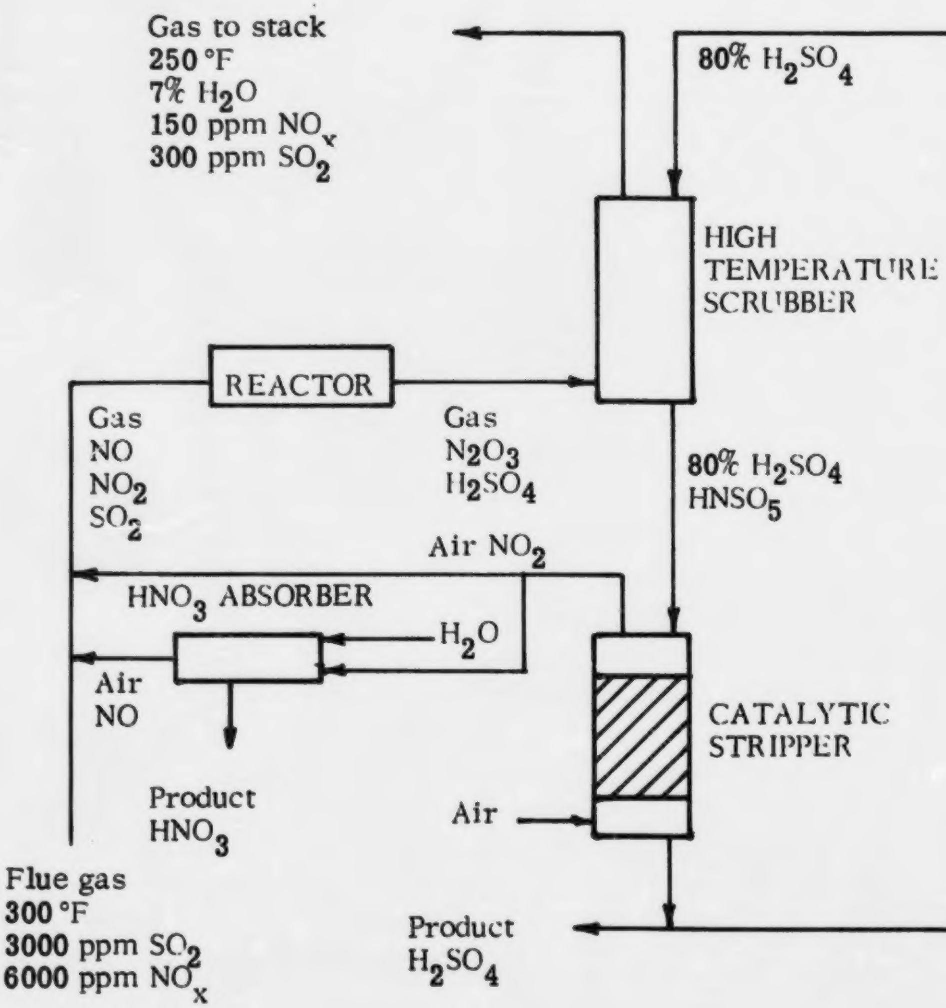
Gas to stack
250 °F
7% H_2O
150 ppm NO_x
300 ppm SO_2
80% H_2SO_4
HIGH TEMPERATURE SCRUBBER
REACTOR
Gas
NO
NO_2
SO_2
Gas
N_2O_3
H_2SO_4
80% H_2SO_4
$HNSO_5$
Air NO_2
HNO_3 ABSORBER
H_2O
Air
NO
CATALYTIC STRIPPER
Product
HNO_3
Air
Flue gas
300 °F
3000 ppm SO_2
6000 ppm NO_x
Product
H_2SO_4

Fig. 1. Catalytic chamber process

This catalytic oxidizer solved two major problems: the reoxidation of the nitric oxide formed in the sulfur dioxide oxidation stage, and the recovery of the oxides of nitrogen from acid solution. This stage was the heart of the process at that stage of development. In combination with the high temperature scrubber, the three shortcomings of the Lead Chamber Process were avoided, thus creating a process which apparently could recover both nitrogen oxides and sulfur dioxide without the need for additional process heat.

The sulfur dioxide was recovered as 80% acid, while the oxides of nitrogen were removed from the off-gas of the catalytic stripper/oxidizer by absorption of nitrogen dioxide in water to form nitric acid. Preliminary cost estimates showed great promise for economic feasibility of the process through the sale of commercial grade acids.

As the contract period covered in this report started, the process as outlined above had been verified in bench scale experimentation as well as preliminary testing of separate process stages in a 10 SCFM "miniplant" (pre-pilot scale). What remained was the integrated operation of the total process and the establishment of engineering criteria for scaleup to pilot level operation at the 2000 to 5000 SCFM level.

The goals of Contract 68-02-0008, therefore, included:

1. Modification of the existing 10 SCFM miniplant to permit integrated operation.

2. Experimentation in the integrated miniplant to determine probable design ranges of critical engineering parameters. A parametric study showing the effect of the various parameters was planned.

3. Preliminary design of a 2000 to 5000 SCFM pilot plant.

4. Evaluation of control levels of SO_2 and NO_x attainable through use of the Catalytic Chamber Process and comparison with desired levels. Goals were 90% removal of SO_2 and 100 ppm of NO_x.

5. Evaluation of the economic feasibility of the overall process and comparison with EPA standards. For the double removal process (both SO_2 and NO_x), the economic goals were an installed cost of under $50/KW with an operating cost of less than 2 mils/KWhr.

6. Other goals included preliminary process control evaluations, determination of a site for the pilot plant, and evaluation of the fly ash problem.

The miniplant was modified to permit integrated operation based on data from previous experimentation. Improvements in sampling and analytical techniques were incorporated. The scrubber (4-in. diameter column) was enlarged to a packed height of 27 ft. The reactor (4-in. dia) was suspended vertically and enlarged to a total of about 15 ft (1.5 ft^3 of volume) in three columns which could be used in series or in parallel. The stripper was also set up in three columns, these being 12 in. in diameter with the packing depth in each being about 35 in. Provisions were again made for a choice of series or parallel operation. Pumps and heaters were installed which could give the operating range required of a complete parametric study.

Initial experimentation involved the determination of operating parameters in the sulfur dioxide reactor stage. It became apparent that the purely gas phase interaction between sulfur dioxide and nitrogen dioxide occurred far too slowly to be feasible. Further testing with improved sampling and analytical techniques established the fact that the fast sulfur dioxide oxidation reaction observed previously was in reality a liquid phase interaction. Re-examination of prior experimentation showed that the liquid phase had always been present in one form or another when rapid reaction rates had been observed. Once this liquid phase reaction was verified, it was possible to modify the concept of the Catalytic Chamber Process to include a stage where the flue gas containing sulfur dioxide contacts a liquid phase consisting of oxides of nitrogen dissolved in sulfuric acid. Extensive experimentation established a maximum residence time of 15 sec being required to remove a minimum of 90% of the sulfur dioxide. Solutions containing 2% wt nitrosylsulfuric acid in 70% sulfuric acid were used to contact flue gas at 225 °F to accomplish this degree of pollutant recovery.

Extensive evaluation of the absorption of equimolar quantities of nitric oxide and nitrogen dioxide in sulfuric acid at elevated temperatures (200-275 °F) revealed that the process is probably a two-step operation and not a simple absorption. Instead of a direct absorption of nitric oxide and nitrogen dioxide into the sulfuric acid, there is apparently a required gas phase reaction between the two gases to form nitrogen trioxide which can then be easily absorbed. This gas phase interaction is relatively slow (compared to the absorption step), and the equilibrium at elevated temperatures and low partial pressures is strongly shifted in favor of the unreacted gases. The result is that long residence times in packed towers are required, thereby greatly enlarging the equipment size.

In estimating the economics of the process, two approaches were taken in sizing the scrubber system: first, the contact in the scrubber would be the same in the full-sized plant as in the miniplant experimentation (a gas mass flow equivalent to about 20% of flooding); and secondly, an assumption that the scrubber could be optimized to approach the industry standard of about 75% of flooding. The marked difference between the capital and operating costs developed by using these two assumptions points out the importance of scrubber size in the overall process.

Using direct scaleup of miniplant data (L/G of 5.0 and a gas mass flow rate of 282 lb/hr-ft^2), an 800-MW power plant producing about 1.5 million standard ft^3/min of flue gas would require a scrubber system, including 106 packed columns 25 ft in diameter and 53 ft high to reduce the NO_x in the effluent to 100 ppm. The total plant cost would be about $413 million or about $500/KW installed. Operating costs would be about $ 96 million or 22.2 mils/KWhr, clearly an impractically high cost. If an assumption of 75% of flooding in the scrubber towers is made, the costs are $114 million and $26.8 million, respectively, for an installed cost of $140/KW and an operating cost of 5.5 mils/KWhr. These latter costs are still very high, but the effect of efficient scrubbing is clearly pointed out. An additional reduction in operating cost can be achieved by selling the product acids: if sulfuric and nitric acids can be sold for $10 and $40/ton (100%), respectively, the operating cost can be reduced by about 1 mil/KWhr.

The scrubber operation was evaluated for nitrogen oxide removal only and was found to be technically feasible, although costly. To reduce the concentration of nitrogen oxides from 2000 ppm to 100 ppm in an 800-MW power-plant, it would take 48 packed towers 25 ft in diameter and 45 ft high if we scaled up directly from miniplant data. The cost of this plant would be about $175 million, with an annual operating cost of about $41 million (8.5 mils/KWhr). Again, assuming that optimization would permit operation at 75% of flooding in the scrubbers, the plant cost could be reduced to $43.5 million and the operating cost to $10.9 million (2.3 mils/KWhr), showing the premium to be gained by improving the scrubber operation.

Evaluation of the catalystic stripper/oxidizer was incomplete because of the emphasis placed on the reactor and scrubber stages. Initial indications were that the oxidation/desorption mechanism may be something other than a liquid phase oxidation of dissolved oxides of nitrogen followed by spontaneous generation of nitrogen dioxide. The presence of carbon dioxide and a large proportion of nitric oxide in the effluent gas at low nitrosylsulfuric acid concentrations (< 0.3%) suggested that the dissolved oxides of nitrogen were being reduced on the carbon (and then oxidizing the charcoal). Some nitrogen dioxide was formed by gas phase oxidation of the nitric oxide, but this reaction is very slow at low nitrose concentrations, and only about 25 to 40% of the total nitrogen oxide content of the stripper off-gas was in the form of the desired nitrogen dioxide. Results in this area are contrary to previously-obtained data at higher nitrose concentrations, and it could well be that operation of the charcoal column under other conditions may cause the necessary liquid phase oxidation.

Preliminary evaluations of process control requirements were initiated during this contract. The first step was to ascertain the operating parameters commonly employed in the power industry. Information obtained included turn-up and turn-down rates, % of excess air, stability of air flow rates, operating changes during equipment failure, and stack effluent properties. Two plants were evaluated: the Astoria, New York unit of Consolidated Edison (primarily oil-fired), and TVA's Chattanooga station (coal-fired). Both showed surprisingly similar operating parameters. In addition, the Brayton Point station (oil-fired) of the New England Power Co. was briefly evaluated, with conditions being generally the same.

A general examination of analytical and control instrumentation was made with the emphasis being placed on response time and operating capabilities. The significant result of this study was that the current state of the art in control instrumentation and equipment is generally compatible with requirements for a process as complicated as the Catalytic Chamber Process. Specific procedures were not developed, but it was felt that there were no problems that could not have been met with current technology.

Discussions were held with Consolidated Edison, TVA, and the New England Power Co. to ascertain the possibilities of building a pilot plant in conjunction with one of their existing power stations. All three expressed interest in pursuing the matter further when the process had achieved a more advanced state of development.

Based on the experimentation and analysis performed during this contract, it would seem that the Catalytic Chamber Process at its current level of development is technologically feasible, but economically impractical. Control levels of 90% removal of SO_2 (from 3000 ppm) and 100 ppm of NO_x can be achieved, but at $125/KW capital cost and 5.5 mils/KWhr operating cost, both at least twice the economic goal. The only future for the process is to improve the operation of the three primary process stages or to develop more advantageous techniques. Recommendations for future work were therefore as follows:

1. Discontinue pre-pilot level experimentation in favor of laboratory bench scale testing.

2. Continue the evaluation of the liquid phase SO_2 oxidation to lower the residence time required for 90% reaction.

3. Re-examine low temperature scrubbing as in the original Lead Chamber Process.

4. Continue evaluation of activated charcoal in the stripper/oxidizer and expand evaluation of previously studied candidate catalysts.

II. INTRODUCTION

A. Content of this Report

This document reports the work performed by Tyco Laboratories, Inc., and its subcontractor, the Badger Corp., during the one-year period February 1971 to February 1972 concerning the development of the Tyco Catalytic Chamber Process for the removal of sulfur dioxide and nitrogen oxides from power plant flue gas. The work was performed under Contract No. 68-02-0008 with the Office of Air Programs (OAP) of the Environmental Protection Agency (EPA). The report will include the experimental and conceptual work accomplished for the evaluation of the engineering feasibility of the process, as well as consideration of the economics involved in the full-scale plant construction and operation.

B. Initial Process Concept

At the start of the contract period covered by this report in February 1971, the Tyco Catalytic Chamber Process had been conceptualized as shown in Fig. 1. The following discussion describes the process as it was pictured at the start of the program and was based on experimental evidence from previous Contract CPA 70-59, as will be given in Part C of this section.

Wet flue gas is mixed with a recycle stream of nitrogen oxides. The mixture undergoes a gas phase reaction in a reactor stage, with the sulfur dioxide being oxidized by nitrogen dioxide (NO_2) to sulfur trioxide which is immediately hydrolyzed to sulfuric acid:

$$SO_2 + NO_2 \rightarrow NO + SO_3 \qquad (1)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (2)$$

The gases containing sulfuric acid and mixed oxides of nitrogen are then passed into a high temperature scrubber where both the product acid and the nitrogen oxides are removed by countercurrent contact with hot sulfuric acid. By operating the scrubber at such a temperature that the vapor pressure of water over the incoming sulfuric acid scrubbing solution is equal to the partial pressure of water in the incoming reacted flue gas (taking into account the small amount of water needed to convert the SO_3 into 80% sulfuric acid), the sulfuric acid and the oxides of nitrogen could be scrubbed out without removing any water from the gas. This prevents the dilution of the scrubbing solution.

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It has been previously established during Contract Nos. PH-86-68 and CPA 70-59 that neither nitric oxide (NO) nor nitrogen dioxide are very soluble in sulfuric acid, but can be readily absorbed as nitrosylsulfuric acid ($HNSO_5$) in the acid if the two oxides are present in equimolar proportions:

$$NO + NO_2 + 2H_2SO_4 \rightarrow 2HNSO_5 + H_2O \qquad (3)$$

Thus, the recycle stream of nitrogen oxides has to be adjusted so that the gas leaving the reactor stage will have equimolar quantities of NO and NO_2.

This technique for the operation of the scrubber stage permits the emission of a gas to the atmosphere, meeting projected standards for SO_2 and oxides of nitrogen. The high temperature operation produces a gas which is buoyant enough to be dispersed in the atmosphere without further reheat.

The nitrated sulfuric acid leaving the scrubber is passed to a catalytic stripper, which simultaneously oxidizes the oxides of nitrogen which have been reduced in the SO_2 oxidation reactor and also permits the complete denitration of the acid without the addition of heat or the dilution of the acid. This is accomplished by the countercurrent contact of the nitrated acid with air on an activated charcoal catalyst:

$$4HNSO_5 + 2H_2O + O_2 \rightarrow 4NO_2 + 4H_2SO_4 \qquad (4)$$

When the reduced portion of the oxides of nitrogen are oxidized back to NO_2, the equimolar balance of NO and NO_2 is upset and the nitrogen oxides are spontaneously evolved. The denitrated acid can then be recycled to the scrubber after an amount of product sulfuric acid equivalent to the amount of SO_2 oxidized in the reactor has been removed.

The gas evolved in the catalytic stripper is then available for recycle back to the entering flue gas to continue the removal of additional SO_2. However, if the scrubber/stripper loop operates at high enough efficiency levels, at this stage there will be excess NO_x in the stripper effluent due to the recovery of additional NO_x from the flue gas. Therefore, a portion of the stripper effluent is passed through a nitric acid absorber, thereby producing additional byproduct acid. The off-gas from the absorber and the remaining effluent from the stripper are then recycled to the flue gas stream.

As given here, the primary advantages of the process are:

1. Both SO_2 and NO_x are removed from dilute flue gas while producing sulfuric and nitric acid as salable byproducts.
2. No additional heat is necessary to operate the process.
3. The process could be added onto existing power stations with only minor modification of existing plant equipment.

C. Prior Work

Previous to this contract, Tyco had developed the process under two contracts with the Department of Health, Education and Welfare: No. PH 86-68-75 and No. CPA 70-59. Details of the work performed can be found in the final reports for these two contracts, and only a summary of the findings will be included here.

Experimentation showed that the original Lead Chamber Process was not adequate for cleaning flue gas because:

1. The required reoxidation of NO simultaneous with SO_2 oxidation by less than stoichiometric quantities of NO_2 in hot, dilute flue gas was too slow to permit reasonable residence volumes.

2. Scrubbing wet flue gas with cold sulfuric acid caused the dilution of the acid, thus requiring additional process heat to effect concentration of the acid.

3. Stripping the cold nitrose required additional process heat.

4. The process required approximately 40% more fuel than the power plant was burning to make up the heat required in (2) and (3) above.

These disadvantages were overcome with the development of the Catalytic Chamber Process which showed that:

1. Scrubbing of NO_x could be effected at high temperatures (in the 250 °F range) and thus avoid picking up water and diluting the scrubbing acid. Experiments performed in a 4-in. tower packed with 3/8-in. Intalox saddles showed 65% removal of NO_x from 7000 ppm concentrations in 8.5 ft of column.

2. Nitrose (nitrosylsulfuric acid in sulfuric acid) could be denitrated by contact with oxygen from air and activated charcoal. In experiments performed at 260 to 290 °F, a 99.7% removal of nitrosylsulfuric acid from nitrose solution (containing 0.7% $HNSO_5$) was achieved in 22 in. of charcoal packing.

3. Reactor experiments showed that about 95% conversion of SO_2 to SO_3 could be achieved at 300 °F and atmospheric pressure, starting with 3000 ppm of SO_2 and about 6000 ppm of NO_2 with a residence time of 15 sec.

4. SO_2 oxidation and NO reoxidation could be effected separately without the need for additional process heat.

D. Contract Goals

The goals of Contract No. 68-02-0008 were to (1) demonstrate process viability by continued operation in an enlarged and integrated 10 SCFM miniplant, including removal of SO_2 and NO_x from simulated flue gas to meet 300 ppm SO_2 and 150 ppm NO_x specifications in exit gas, (2) establish process and engineering data for scaleup to a 2000 to 5000 SCFM pilot plant level along with potential site locations, and (3) update process economics.

More specifically, the work was to include the following tasks:

1. Develop engineering data for the SO_2 oxidation reactor design. The reactor was to be run separately from the rest of the miniplant to include optimization of reaction, temperature, and residence time to achieve 90% conversion yield starting with 3000 ppm SO_2 in the incoming gas.

2. Develop design criteria for the NO_x scrubber and catalytic stripper. The scrubber and stripper were to be operated without the reactor to establish the following operating parameters in a statistically designed parametric study:

a. Scrubber height necessary to reduce the 7000 ppm NO_x level to 150 ppm (also the height of a theoretical transfer unit). [Note: Approximately 600 ppm NO_x are present in the initial flue gas from the power plant furnace. The remainder results from recycle of the NO_2 to the reactor.]

b. Temperature range for scrubber operation

c. L/G for scrubber

d. L/G for stripper

e. Stripper catalyst bed depth

f. Stripper gas and acid space velocities

g. Stripper operating temperature

h. Excess air to stripper.

3. Operation of the integrated miniplant, using a statistically-designed experimental study of major process operating variables. Of particular importance is process control and process sensitivity near optimum conditions, corrosion tests, and the effect of fly ash contamination through simulated study.

4. Development of process control criteria. A preliminary evaluation of process control considerations was to be made based on the original process, as given in Section II. Such items as the availability of in-line analytical instrumentation, techniques of fluid flow and concentration adjustment, control equipment, response time requirements, and power plant operating procedures were to be determined. A process control system would be recommended.

5. Selection of a site for subsequent 2000 to 5000 SCFM pilot plant installation. Discussions were to be held with utility companies such as Consolidated Edison Company of New York, the Tennessee Valley Authority, and other interested utilities to examine the possibility for locating a pilot plant on the site of an existing power station.

6. Prepare a preliminary design for a pilot plant.

In conjunction with a subcontractor, the Badger Corp., a preliminary pilot plant was to be designed based on the engineering criteria developed in the experimental phases of the contract. The plant design would hopefully be tied to a specific location and a specific stack gas.

III. ENGINEERING SUBCONTRACTOR — THE BADGER CORPORATION

The Badger Corporation was engaged as subcontractor to Tyco for the purpose of providing additional expertise in the areas of engineering and design. Badger's role in the contract was designed to be in three areas: (a) general engineering consultation, (b) design of a computer program for process optimization, and (c) preliminary design of a 2000 SCFM pilot plant.

A. Engineering Consultation

During the early stages of the contract, Badger's primary function was to evaluate the process from a plant design viewpoint and help in the design of experimentation which would help develop the data needed for the preliminary pilot plant design. Several meetings were held between Tyco and Badger personnel to exchange information and develop ideas for experimentation. In this area, Badger made an initial evaluation of the process and made general suggestions given in Appendix I.

B. Optimization Program

Badger utilized their extensive experience in computer optimization of process variables in chemical plants to develop a program which was intended to help in the analysis of the experimental data. Based on the process conceptualization given in Part I of this report, a program was written around process stoichiometry which would permit optimization of the operating variables. As new experimental data was reported, the process concept was revised and the program was appropriately modified. In this manner, the program could be used to back up the experimental work and keep the laboratory and miniplant work aimed in the proper direction. As the contract orientation shifted from plant design to reevaluation of process concepts, the optimization work was deemphasized. At the completion of the contract, Badger had a partially modified program which would require several changes to be useful for further optimization.

C. Pilot Plant Design

During the early stages of the contract, Badger's major contribution in the pilot plant design area was to provide assistance in developing the process control system that could be used with this type of process. This work will be discussed in some detail in Section VIII of this report. During the latter stages of the contract, it became clear that the process concept was not sufficiently developed to permit pilot plant design, and this phase of the work was discontinued.

IV. MINIPLANT MODIFICATION AND EQUIPMENT

A. Existing Equipment

At the start of this contract, the all-glass miniplant used in Contract No. CPA 70-59 was operable, but needed extensive modification to permit complete evaluation of the process variables. The previous contract had established revised operating parameter ranges for important variables, and it was therefore necessary to change the capacity of certain process stages to accomplish suitable integrated operation. The SO_2 oxidation reactor, the scrubber system, and the stripper stage all had to be modified and enlarged, which created the need for changes in pumps, flowmeters, piping systems, and instrumentation. Fig. 2 shows the flowsheet of the miniplant as conceived at the beginning of this contract in February 1971. As the contract proceeded, several additional modifications were required, and they will be discussed in the following sections of the report.

B. SO_2 Oxidation Reactor

The reactor used in the prior contract was a horizontal glass tube, 4 in. in diameter and about 5 ft long. Experimentation during the previous contract indicated that the oxidation of SO_2 to SO_3 (with subsequent hydration to H_2SO_4) might not be as simple as the equation $SO_2 + NO_2 = SO_3 + NO$ would suggest. The reactor in the miniplant was therefore designed so that this reaction could be examined in more detail than in the past. The reactor was placed in a vertical configuration and its size increased from about 0.5 ft^3 to about 1.5 ft^3, with the option existing for using either one-third of the new reactor or the whole volume. The first third of the reactor was set up so that it could be easily packed, if necessary, with some material for increasing surface area and possibly to spray the gas with a fine acid mist. Later, an option was made available for a single 15-ft reactor column to be installed in series with a liquid phase feed system. The spray capability was added to simulate the conditions in the chambers of the Lead Chamber Process Plant and thus evaluate the possibility that some phase of the oxidation involved a liquid phase reaction. The reactor was assembled using a 4-in. glass pipe and jacketed for heating the simulated flue gas. Previous experience indicated that a maximum temperature of 375 °F could be achieved in the reactor column.

C. Scrubber Columns

As shown in Fig. 2, the initial plant operation was to utilize a single glass scrubber

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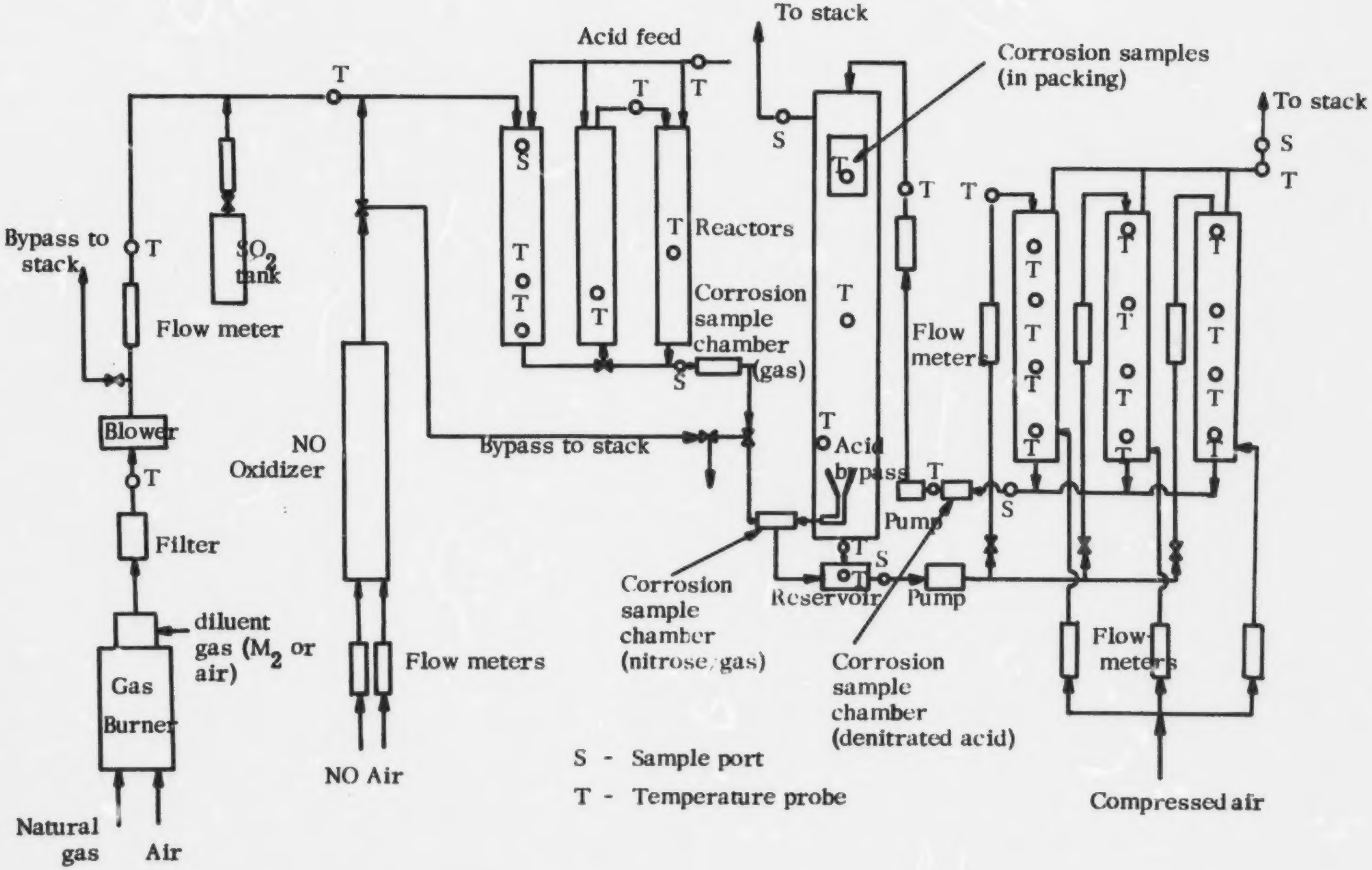

To stack
Acid feed
Corrosion samples
(in packing)
To stack
T
S
T
Bypass to stack
SO_2 tank
Flow meter
Reactors
Corrosion sample chamber (gas)
Flow meters
Blower
NO Oxidizer
Bypass to stack
Acid bypass
Pump
Filter
Corrosion sample chamber (nitrose/gas)
Reservoir
Pump
diluent gas (M_2 or air)
Gas Burner
Flow meters
Corrosion sample chamber (denitrated acid)
Flow meters
NO Air
Natural gas
Air
Compressed air
S - Sample port
T - Temperature probe

Fig. 2. Schematic flowsheet of miniplant (strippers in parallel configuration)

column containing about 7.5 ft of packing (3/8-in. Intalox saddles). This column was similar to the one used in the prior contract, and it was known that scrubbing efficiencies in excess of 65% could not be achieved in a column of this height. During the contract period, it was therefore decided to enlarge the scrubbing system by adding an additional glass column containing 19 ft of packing. A sketch of this column is shown in Fig. 3. All scrubbing experimentation was performed using the two scrubbers (7.5-ft and 19-ft sections) in series.

D. Stripper Columns

In order to achieve stripper space velocities equal to those used in the laboratory experimentation performed in Contract CPA 70-59, the stripper stage was redesigned to consist of three 4 ft high × 12-in. diameter columns operated in parallel (see Fig. 2). The catalyst was Witco Type 256 activated charcoal 4 × 10 mesh.

As initially designed, the stripper columns consisted of Teflon-coated, stainless steel tubes as shown in Fig. 4. The tubes had gas feed ports at two levels and four ports for thermowell probes on the sides. There were two openings in the top cover (acid feed and gas exit) and an acid drain in the bottom. Ports which connected to transfer lines were flanged using standard 150 lb ASA dimensions for easy connection to 1-in. glass pipe. All surfaces which were to come into contact with acid were coated with Teflon.

Inside the tubes provisions were made to support four beds of activated charcoal. Three-pronged spiders, resting on half-inch studs welded to the inside wall at four levels, provided support for the center sag of the fiberglas fabric-wrapped ring which was the actual support plate for the charcoal. A sketch of this arrangement is also shown in Fig. 4. The three strippers were each loaded with approximately 25 lb of charcoal to a depth of about 35 in.

During the operation of the system, it became obvious that the coating was not adhering properly to the surface of the column and the metal was corroding severely (note Appendix VI). The three columns were cleaned and recoated with another Teflon formulation recommended by duPont, but this coating eventually failed also. Rather than continue to experiment with other coatings, it was decided to redesign the strippers to use an all-glass system with solid Teflon gaskets and covers. A sketch of this new design is shown in Fig. 5.

This design made use of a glass packing support plate perforated with half-inch holes. To prevent the activated carbon from falling through the holes, the support plate was covered with a thin Teflon sheet perforated with quarter-inch holes. A layer of 3/8-in. saddles was placed over the Teflon plate and the carbon placed on top of the saddles. During several weeks of operation there was no apparent loss of carbon particles (which were 4 × 10 mesh). This support design avoided a problem that arose with the fiberglas fabric support configuration. In the earlier design the fine holes of the fiberglas fabric created such a high pressure drop that the air pressure required to force air up the column prevented the uniform flow of acid down the column. The new design had no such high pressure drop and uniform flow was easily achieved.

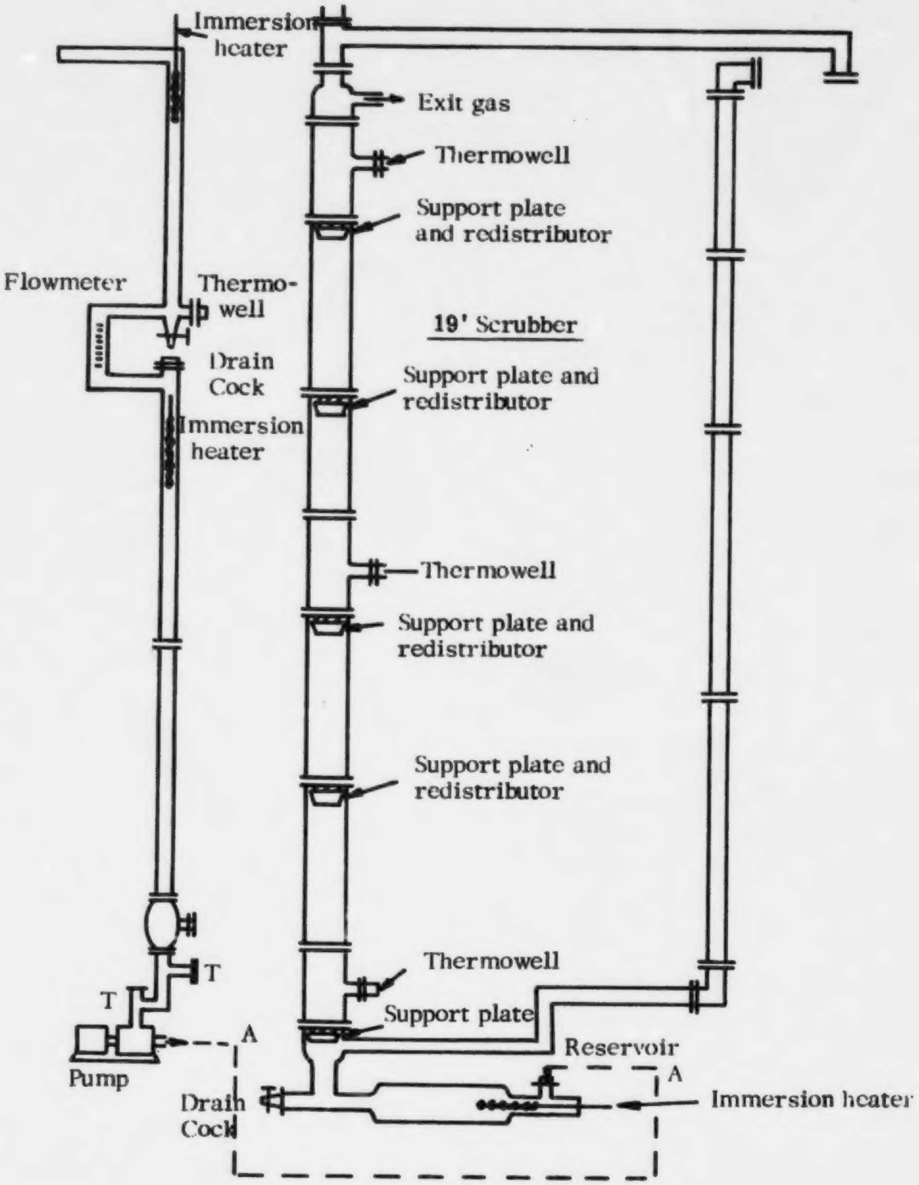

Immersion heater
Exit gas
Thermowell
Support plate and redistributor
Flowmeter
Thermo-well
19' Scrubber
Drain Cock
Support plate and redistributor
Immersion heater
Thermowell
Support plate and redistributor
Support plate and redistributor
Thermowell
T
T
Support plate
A
Reservoir
Pump
A
Drain Cock
Immersion heater

Fig. 3. Sketch of 19-ft scrubber

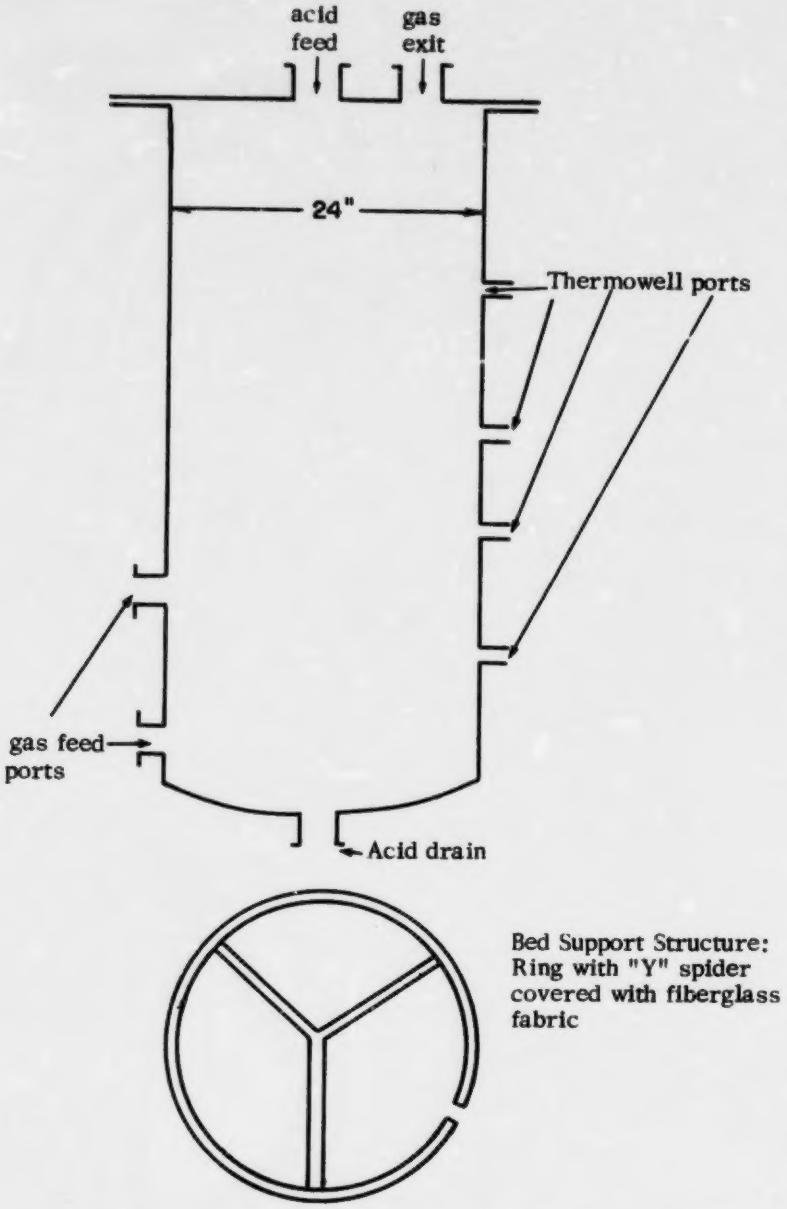

acid feed
gas exit
24"
Thermowell ports
gas feed ports
Acid drain
Bed Support Structure: Ring with "Y" spider covered with fiberglass fabric

Fig. 4. Miniplant stripper column and catalyst bed support structure

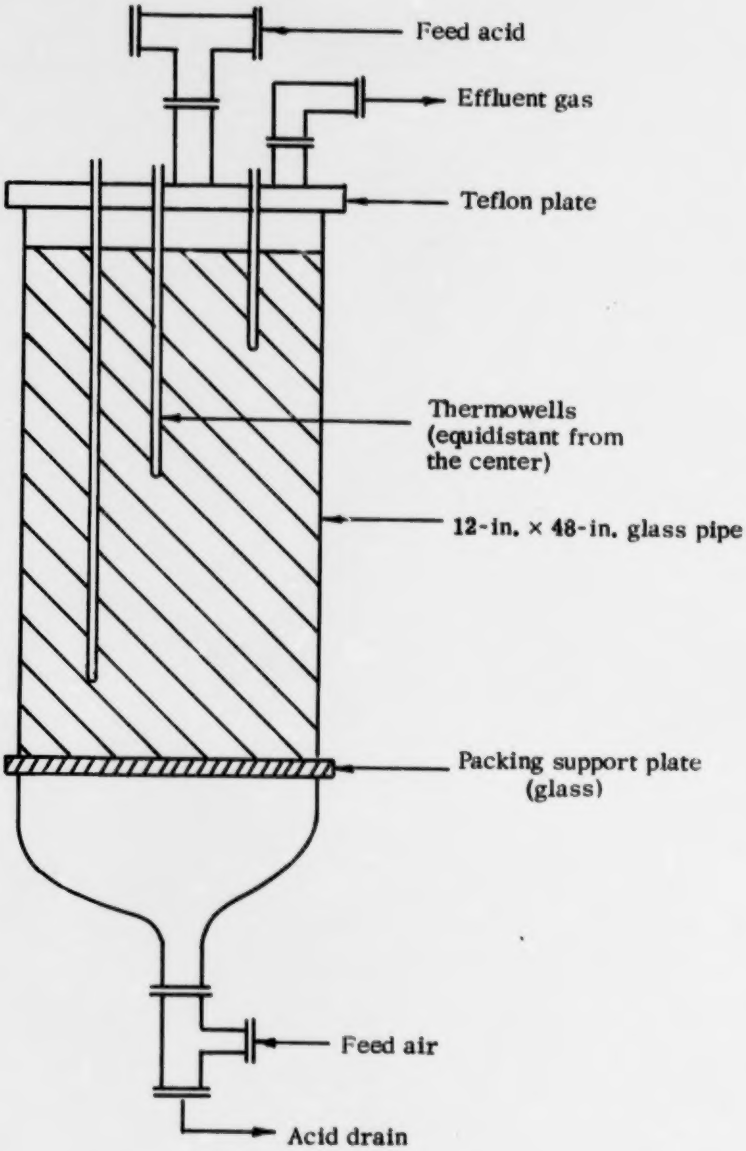

Feed acid
Effluent gas
Teflon plate
Thermowells (equidistant from the center)
12-in. × 48-in. glass pipe
Packing support plate (glass)
Feed air
Acid drain

Fig. 5. Stripper column using glass pipe

E. Liquid Pumps

During earlier work on the miniplant in Contracts PH 86-68-75 and CPA 70-59, the acid had been pumped through the system using piston pumps of standard design (Clark-Cooper Mark II Metering Pump), with all wetted parts being made of Carpenter 20 alloy. These had required considerable maintenance, and new pumps were ordered for this contract.

All Teflon pumps (Fluorocarbon Co. Saturn Pump) utilizing a nutating disc design were used during the early stages of the contract, but these too were unsatisfactory. The major problem with this design was the softening of the Teflon at high temperatures which caused the internal seal to leak, thus reducing flow to a trickle. These pumps also had a tendency to foul easily, and small particles prevented a good seal between the nutating disk, thus sharply reducing its flow.

The Saturn Pumps were replaced with ECO gearpumps utilizing Hastelloy B construction to prevent corrosion. Estimates by both Tyco and ECO indicated that Hastelloy B was a marginal material of construction for long term use, but should be adequate for the duration of the contract (about 50 mils/yr corrosion level). In actual use, however, excessive aeration of the acid combined with the high temperature, high speed operation of the pump caused erosion of the pump body. This resulted in excessive clearance around the gears which reduced the acid flow to very low levels.

The pumps that eventually proved adequate to the task of pumping 80% sulfuric acid at temperatures over 200 °F were simple peristaltic pumps manufactured by the Ober Co. for Cole-Parmer. The Masterflex Pump using Viton tubing could be used for up to about 36 hr before tubing replacement was required. This meant that complete runs could be made without interruption for pump maintenance, and even if tubing replacement was required, the changeover only took a few minutes and thus avoided long periods of down time. This certainly was not a long term answer to the pumping problem for either the miniplant or the larger pilot plant, but was certainly adequate for the short term requirements of this contract.

It was interesting to note that on a larger scale, pumps are readily available that can handle the operating conditions of this system. The Durco Co. manufactures duririon centrifugal pumps in sizes which can handle pumping rates of 5 to 3000 gpm. However, the centrifugal pumps could not easily handle the 0.1 to 0.8 gpm required in the miniplant, and smaller pumps made of duririon are not available.

F. Gas Pumps

The miniplant had two requirements for pumping of gases: transferring the raw simulated flue gas, and pulling a gas sample from various points in the process gas loop. The first requirement had been met in the original miniplant design by using a blower manufactured by MGD Pneumatics Co. This blower easily provided up to 12 SCFM of raw flue gas.

The sample pump was a far more difficult problem because of the combination of high temperature, high water content, and the corrosive nature of the gas. After trying several pumps which proved inadequate, a low cost diaphragm pump made by Bell & Gossett (Fluid

Handling Div., I.T.T.) was chosen. This pump required relatively frequent maintenance, but the low cost of the unit permitted the use of several spares which could be kept ready for rapid installation while the fouled pump was cleaned. By carefully trapping condensed liquid in the gas lines, the pump could be operated for several days without problems.

G. Instrumentation

Instrumentation in the miniplant involved three areas: flow rate determination, temperature measurement, and in-line gas analysis. No automatic control equipment was used. Fig. 6 shows the miniplant after final modifications and sample point installation.

1. Flow rate determination

All liquid and gas flow rates were measured using in-line glass rotameters as shown in Fig. 6. Liquid levels in reservoirs and columns were controlled by visual inspection and throttle valve adjustment by the plant operators.

2. Temperature measurement

Over forty temperature measurement points were utilized to help monitor and control the process. Two Esterline Angus twenty-four point recorders were therefore installed to continuously monitor the temperature levels, with the data being extracted from the recorder printout by the plant operator and recorded permanently on data sheets.

3. Gas analysis

At several points in the system, the process gas lines were monitored for concentration of NO_2, SO_2, and NO. This was accomplished for the first two gases by analysis with a duPont Model 400 ultraviolet photometer. Nitric oxide was monitored with a Beckman Model 315A infrared analyzer. In addition, the water content of the gas was periodically monitored with a EG&G Model 2000 dew point hygrometer.

H. Gas Feed

The flue gas feed was simulated by doping the effluent of a natural gas burner with sulfur dioxide as shown in Fig. 6. The exhaust gas from the burner was diluted with air to reduce the water content of the flue gas fed to the system so that the feed stream contained about 6% water, 15% oxygen, plus CO_2 and nitrogen. Sulfur dioxide was metered into the controlled exhaust gas stream to create any desired concentration.

Nitrogen dioxide was fed to the system by oxidizing nitric oxide with air. NO_2 is a liquid below 22 °C and is very hard to handle around room temperature. Previous experience had shown that the gas condensed in flow meters and tubing creating a very difficult cleanup problem. In order to avoid this problem a large empty reactor chamber was used to oxidize the NO to NO_2 before it was fed to the process. Yields of 75 to 85% were obtainable in this manner. See Appendix X for a discussion of air oxidation of NO for this application.

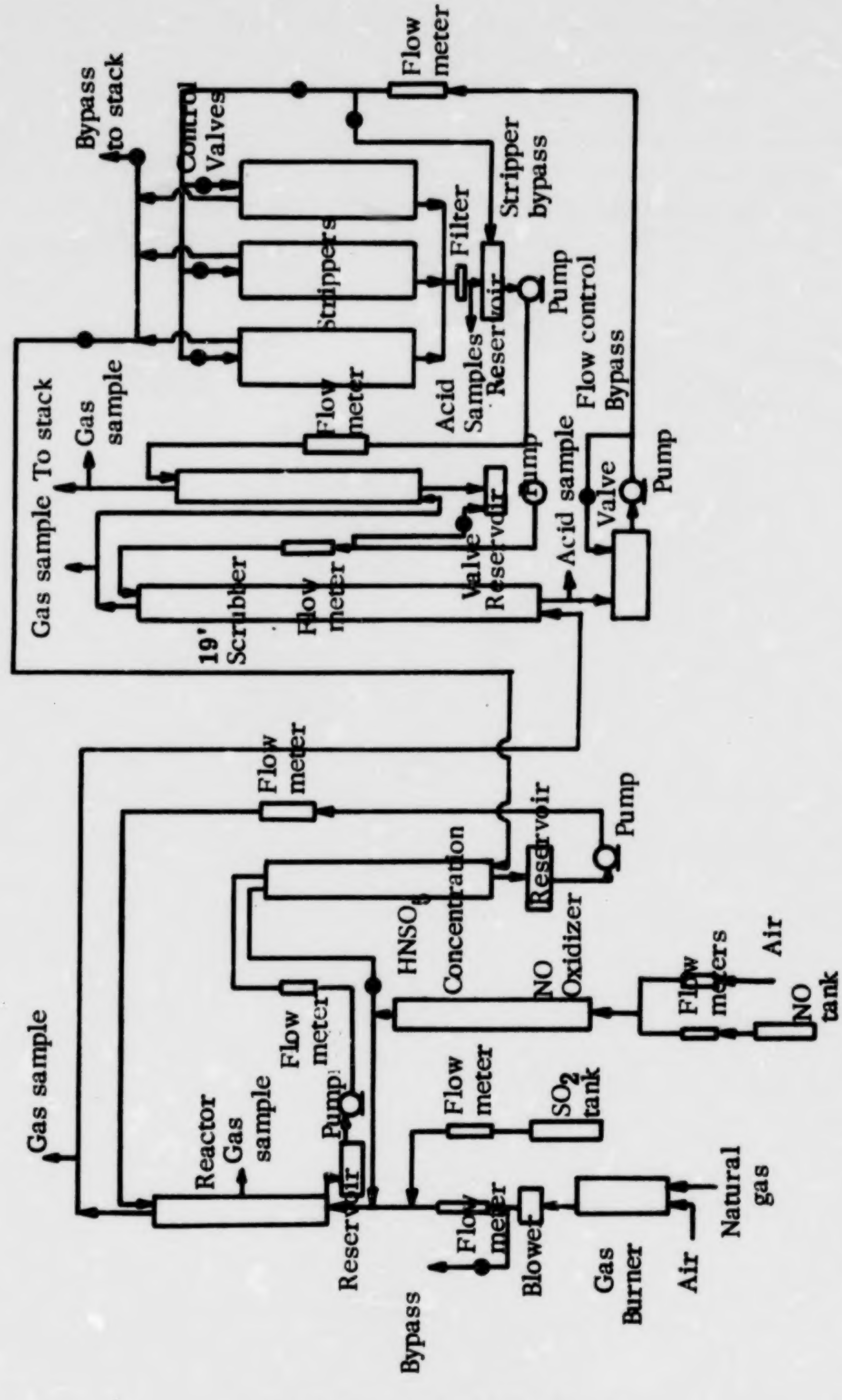

Bypass to stack
Control Valves
Flow meter
Strippers
Filter
Stripper bypass
Reservoir
Pump
Acid Samples
Flow control Bypass
Gas sample
To stack
Gas sample
Flow meter
Pump
Reservoir
Acid sample
Valve
Pump
Gas sample
19' Scrubber
Flow meter
Valve
Reservoir
Flow meter
Pump
Reservoir
HNSO$_5$ Concentration
NO Oxidizer
Flow meters
Air
NO tank
Gas sample
Reactor
Gas sample
Flow meter
Pump
Reservoir
Flow meter
SO$_2$ tank
Flow meter
Blower
Gas Burner
Air
Natural gas
Bypass

Fig. 6. Modified miniplant layout

I. Miniplant Operation

The approach taken during the contract was to operate the miniplant in separate stages leading up to integrated operation. First, the reactor stage was fully evaluated and then the scrubber/stripper loop was investigated. The emphasis in plant design was on simplification of operation to aid in the rapid accumulation of data. This was particularly pertinent since the miniplant was operated by two men per shift. Details of the miniplant operation, including data-taking procedures, gas sampling techniques, and mode of shift operation are presented in Appendix II.

V. REACTOR EXPERIMENTS

A. Background

Experimentation on Contract CPA 70-59 indicated that the gas phase oxidation of SO_2 with NO_2 occurred very rapidly at 300 °F such that at a concentration of 3000 ppm SO_2, about 95% would be converted to H_2SO_4 in less than 20-sec residence time. These results were somewhat erratic, but several runs were made that gave consistant yields at this level. The only reason for questioning the data was the fact that the residence time of the gas in the sample lines and analyzer was about 15 of the total 20-sec contact time. To verify this earlier data, a series of experiments was run in the miniplant using a three-reactor column containing about 1.6 ft^3 of volume. The gas sample system was modified so that the gases were in contact for only about 2 to 4 sec in the sample lines, and the results more closely represented the reaction occurring in the reactor chamber.

Initial tests at 300 to 350 °F, using gases containing about 3000 ppm of SO_2 interacting with NO_x streams providing about 6000 ppm of NO_2 and about 2000 ppm of NO, indicated reaction rates of about 15 to 20%, with reactor residence time of 15 sec and sample line residence times of about 3 sec. Table I shows some of the data from these initial runs. These low yields necessitated a more complete evaluation of the reactor system due to the differences between the experimental system used in the earlier tests and the more recent miniplant and sampling system design.

Clearly, the most significant of these differences was the shorter sample line residence time although the total contact time was about the same. In addition, the sample lines were modified so that heating was more uniform and condensation in the lines was greatly reduced. Rather than using 1/4-in. glass pipe wrapped with heating tapes, the samples were pumped through 3/16-in. Teflon tubing which was enclosed in aluminum tubing wrapped with heating tapes. This approach avoided the flanged sections of pipe which were very hard to wrap with tapes and permitted continuous lengths of uniformly heated tubing which could be easily cleaned.

To evaluate the effect of these plant modifications as well as examine the operating parameters of the reactor, a series of miniplant reactor tests were run as discussed below.

B. Reactor Experiments: Effect of UV Radiation

Initially, two experiments were run to determine if UV radiation accelerated the gas phase reaction between SO_2 and NO_2. An empty 4-in. glass column containing 0.53 ft^3 of void

Table I. Initial Reactor Studies

	Run 4	Run 8	Run 8A
Reactor temperature (°F)	350	350	300
Gas flow rate (SCFM)	4	4	4
Gas feed: (ppm)			
SO_2	3200	3050	2950
NO_2	6100	6000	6000
NO	1700	1400	—
H_2O (%)	~6.0	~6.0	~6.0
Effluent gas: (ppm)			
SO_2	2750	2600	2300
NO_2	6050	6700	5350
NO	2200	1800	2400
Reactor residence time (sec)	14.5	14.5	15.5
Sample line residence time (sec)	~3	~3	~3
Reactor volume (ft^3)	1.6	1.6	1.6
SO_2 removal efficiency (%)	14.1	14.8	18.7

volume (6 ft long) was modified so that a UV source emitted radiation down the length of the tube. Gas containing SO_2, NO_2, and NO was fed into one end of the column (the end housing the UV source), and the gas concentration was monitored before and after passing through. Two runs were made, as shown in Table II, with the only difference between the two runs being that in Run 51 the radiation was directed toward the side of the column and was reflected through the tube by aluminum foil. In Run 51A, the source was aimed along the length of the tube. In both cases, the radiation passed through a quartz plate which protected the source from the corrosive gases.

It is clear from the results of the two runs that the UV radiation had no effect on the oxidation rate of the SO_2 by NO_2. Although there is a consistent NO_x material balance error due to small NO_x analysis errors, there is no apparent acceleration of the oxidation of SO_2.

C. Miniplant Tests: Effect of Temperature on SO_2 Oxidation Rate

During the early runs, discussed above, there were indications that temperature had a significant effect on the SO_2 oxidation rate. To evaluate this effect, the reaction was tested over a range of temperatures at different flow rates in order to vary the reactor residence time. At the same time, the effect of water vapor in the gas stream on reaction rate was evaluated by running the tests with and without the gas burner. It should be noted that the primary purpose of the gas burner was to introduce water through the oxidation of natural gas. The gas burner effluent contained about 6% water after dilution. The results of these tests are shown graphically in Fig. 7.

It had been anticipated that the gas phase oxidation of SO_2 with NO_2 proceeded according to the reaction:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

and would proceed at a faster rate at higher temperatures. The data in Fig. 7 show that just the opposite was true: higher temperatures brought about lower oxidation rates. The data also showed that at lower temperatures the presence of water vapor in the reaction stream was essential to higher reaction rates.

In general, the results were more compatible with a mechanism involving a liquid phase reaction rather than the expected gas phase oxidation. The increasing reaction rate at lower temperatures suggested the necessity of dissolving the gas phase reactants in a liquid phase before the reaction could take place. Comparing the Tyco Process with the original Lead Chamber Process, it should be noted that one major difference is the absence of liquid addition in the SO_2 reaction stage. Much has been written about the complexity of this reaction, and at this stage of experimentation it appeared that the liquid phase addition might well be essential to high reaction rates.

D. Effect of Acid Irrigation on SO_2 Oxidation Rate

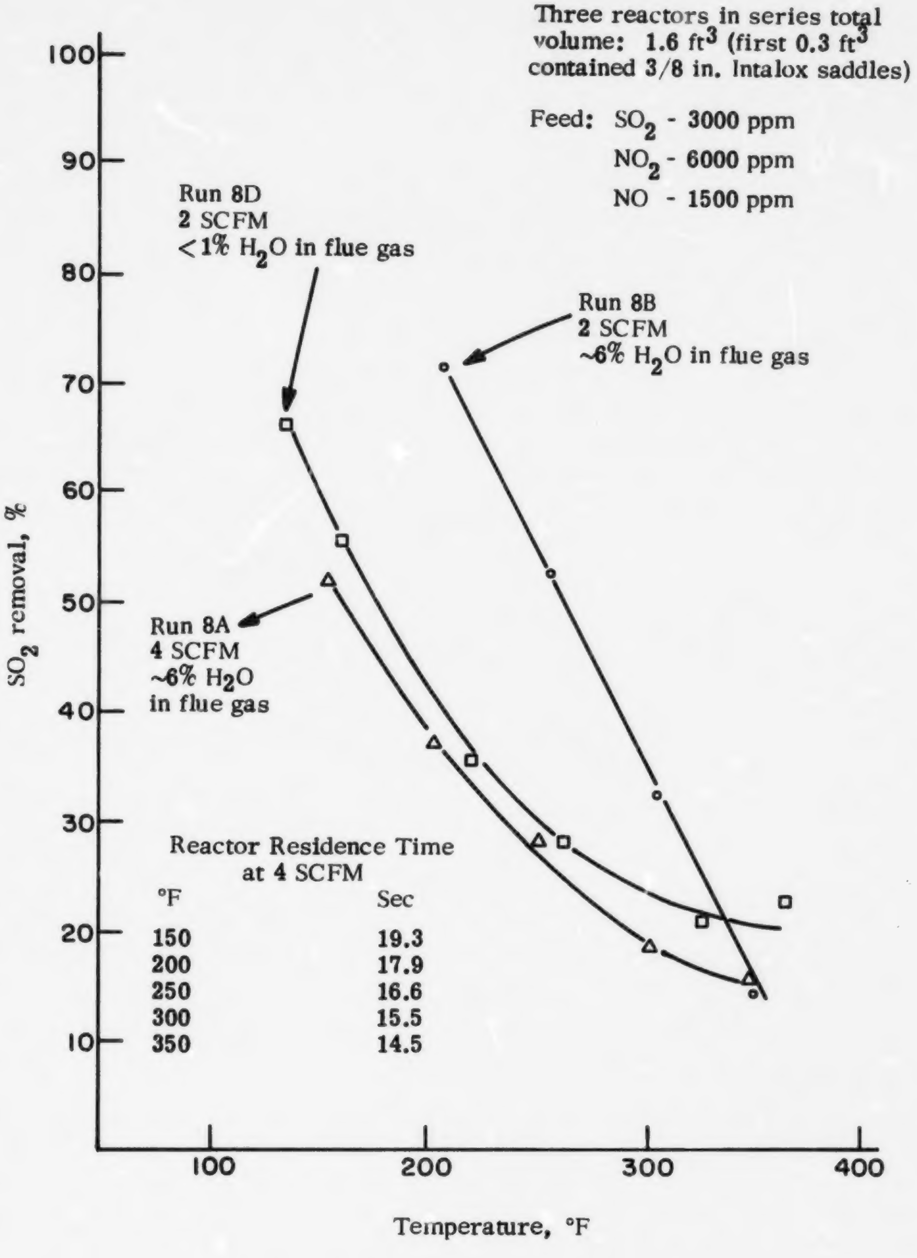
To evaluate this concept, a series of experiments was performed in the miniplant reac-

Table II. Gas Phase SO_2 Oxidation with NO_2 in the Presence of UV Radiation

	Run 51	Run 51A
Gas flow rate (SCFM)	2	2
Column temperature (°F)	250	250
Gas feed: (ppm)		
SO_2	2800	3400
NO_2	5600	6200
NO	1500	1900
Effluent gas: no UV (ppm)		
SO_2	2000	3100
NO_2	8600	9050
NO	1675	3850
Effluent gas: with UV (ppm)		
SO_2	2050	3100
NO_2	8500	9050
NO	1775	3850
SO_2 removal without UV (%)	28.6	8.9
SO_2 removal with UV (%)	26.8	8.9

Notes:

1. Run 51A was run under identical conditions to Run 51 except that the UV source was aimed directly down the reactor column instead of into the wall.
2. Reaction run in empty glass tube 4 in. × 72 in. (0.53 ft^3).



Three reactors in series total volume: 1.6 ft^3 (first 0.3 ft^3 contained 3/8 in. Intalox saddles)

Feed: SO_2 - 3000 ppm
NO_2 - 6000 ppm
NO - 1500 ppm

Reactor Residence Time
at 4 SCFM

°F	Sec
150	19.3
200	17.9
250	16.6
300	15.5
350	14.5

Fig. 7. Miniplant reactor experiments – SO_2 oxidation. Effect of water vapor in flue gas, residence time, and temperature

tor which was modified to permit irrigation of part of the chamber with a liquid phase. Fig. 8 shows the configuration of the reactor during this phase of experimentation. The diagram shows that the gas could be passed through either one reactor chamber (0.64 ft^3 containing 0.3 ft^3 of 3/8-in. Intalox saddles) or three chambers (1.52 ft^3 total), with only the first reactor chamber being irrigated. The saddles were placed in this chamber to increase the gas/liquid contact.

Figs. 9 and 10 show the results of irrigating the first reactor section (containing the saddles) with 80% sulfuric acid at gas flow rates of 2 and 4 SCFM. It is clear that there is no apparent advantage to acid irrigation under the conditions shown. Fig. 10 also shows the effect of irrigating the first reactor section with water rather than acid. Because of the vaporization of water above 150 °F, it was impossible to continue the experiments above this temperature, but if the effect could be extrapolated to higher temperatures, it would appear that again there would be little advantage.

During some of the irrigation runs, it had been noticed that, if the acid had been exposed for a period of time to NO_x in the gas phase before the SO_2 was introduced into the flue gas, the initial reaction rate was significantly higher than the eventual steady state reaction level. This led to the concept involving the buildup of dissolved NO_x in the liquid phase in order to effect high reaction rates. To test this hypothesis, the column was irrigated with acid for an extended period of time, after which the acid flow was stopped. The gas phase reactants were then introduced into the reactor and the effluent concentrations allowed to achieve steady state. Fig. 11 shows the results of this test at 2 SCFM. Clearly, this technique is far superior to either the dry reaction mode or the continuous acid irrigation.

Examination of Fig. 11 reveals an anomaly which should be considered at this point. The experiment which involved the continuous irrigation of the reactor with 80% sulfuric acid exhibited lower reaction rates than the dry interaction, which apparently contradicts the proposed liquid phase reaction mechanism. This can be explained in terms of the actual conditions in the reactor during most of the experimentation. The tests described up to this point were usually run for a few hours at the most and one right after the other. The net effect is that the "dry" condition mentioned above was very rarely the case. Even when running without irrigation, it took many hours for the saddles to be completely dried out from either previous runs or condensation during unirrigated runs. It is therefore quite likely that, during the "2 SCFM, burner on, no acid" run shown in several of the graphs, there was a significant amount of acid present on the saddles which improved the reaction due to buildup of reactant concentration in the liquid phase. The extreme of this wetted condition is undoubtedly shown by the top curve in Fig. 11.

One more series of tests was run to ascertain the advantage of the presence of a liquid phase. This involved two runs in which the saddles in the first section of the reactor were wetted with 80% sulfuric acid before the reaction was initiated. In one of the two tests, the gases were passed into the other two void sections of the reactor before analysis, while in the second test the effluent gases from the packed section were analyzed immediately. The

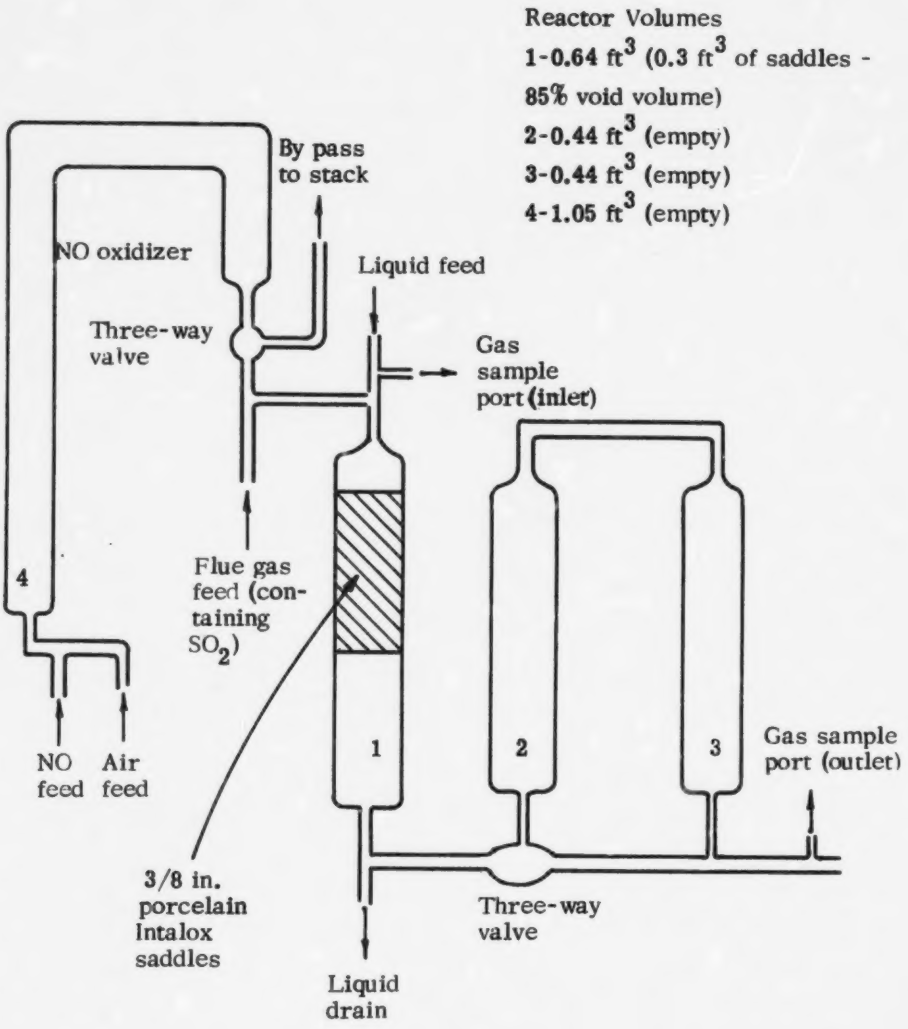

Reactor Volumes
1-0.64 ft^3 (0.3 ft^3 of saddles - 85% void volume)
2-0.44 ft^3 (empty)
3-0.44 ft^3 (empty)
4-1.05 ft^3 (empty)
By pass to stack
NO oxidizer
Liquid feed
Three-way valve
Gas sample port (inlet)
Flue gas feed (containing SO_2)
4
1
2
3
Gas sample port (outlet)
NO feed
Air feed
3/8 in. porcelain Intalox saddles
Three-way valve
Liquid drain

Fig. 8. Configuration of miniplant reactor during initial experimentation involving liquid irrigation

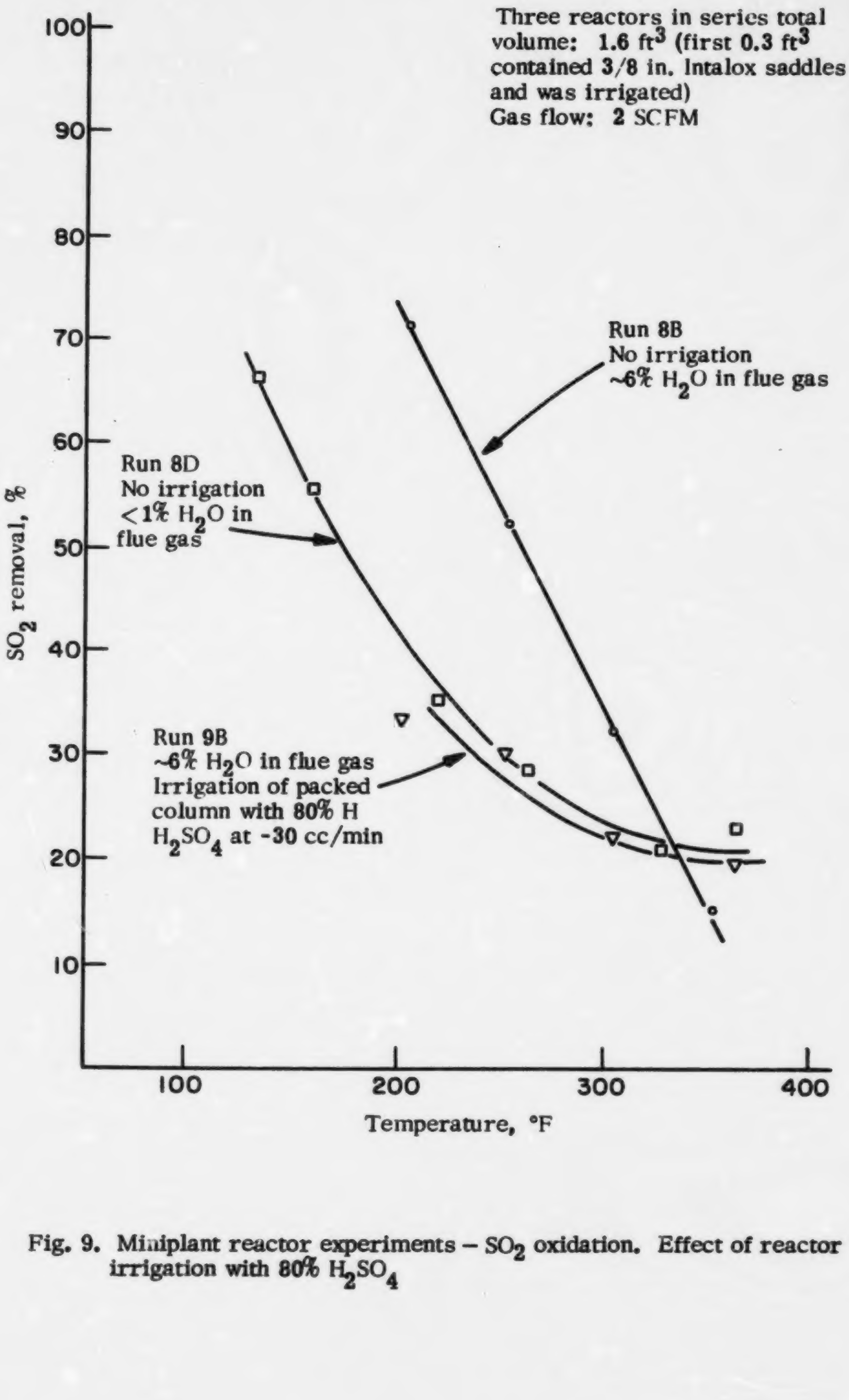


Fig. 9. Miniplant reactor experiments – SO_2 oxidation. Effect of reactor irrigation with 80% H_2SO_4

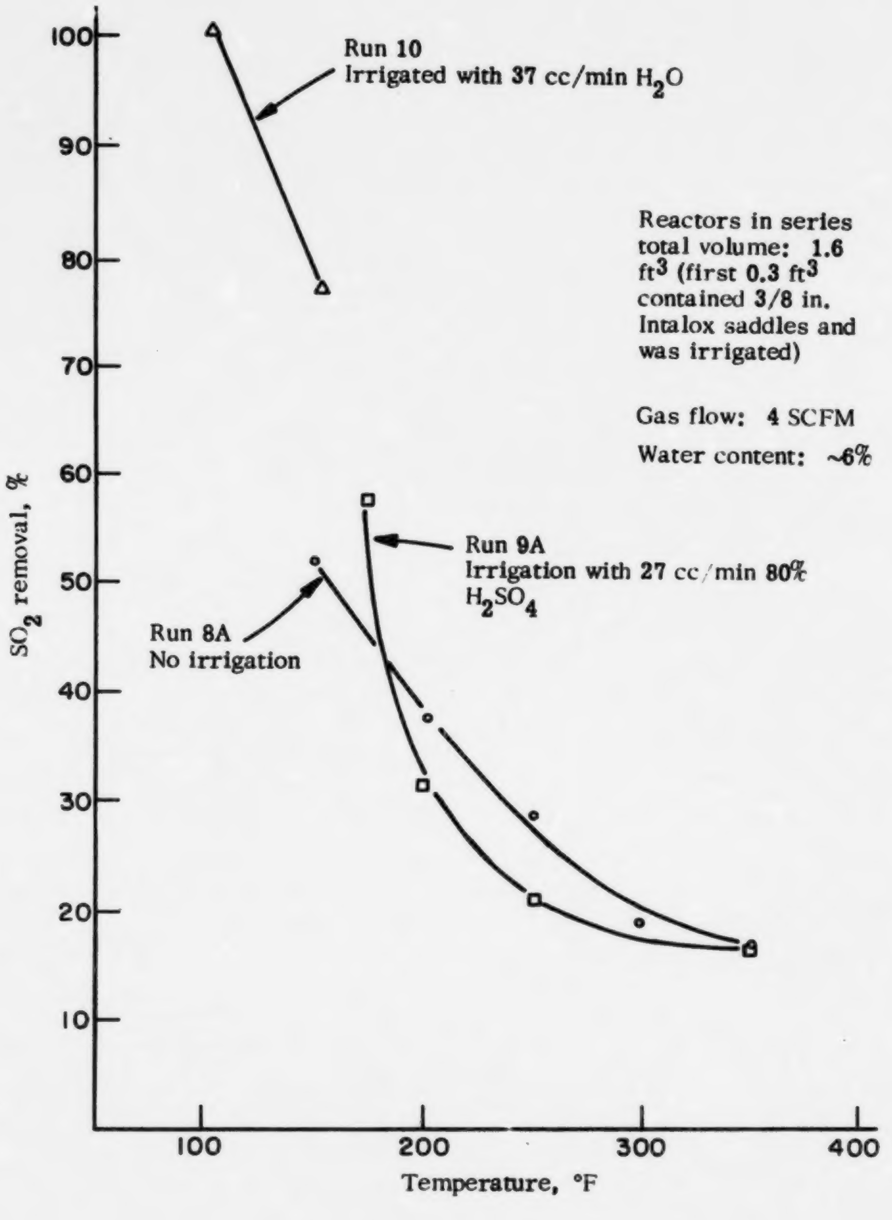


Fig. 10. Miniplant reactor experiment – SO_2 oxidation. Effect of acid or water irrigation in packed reactor

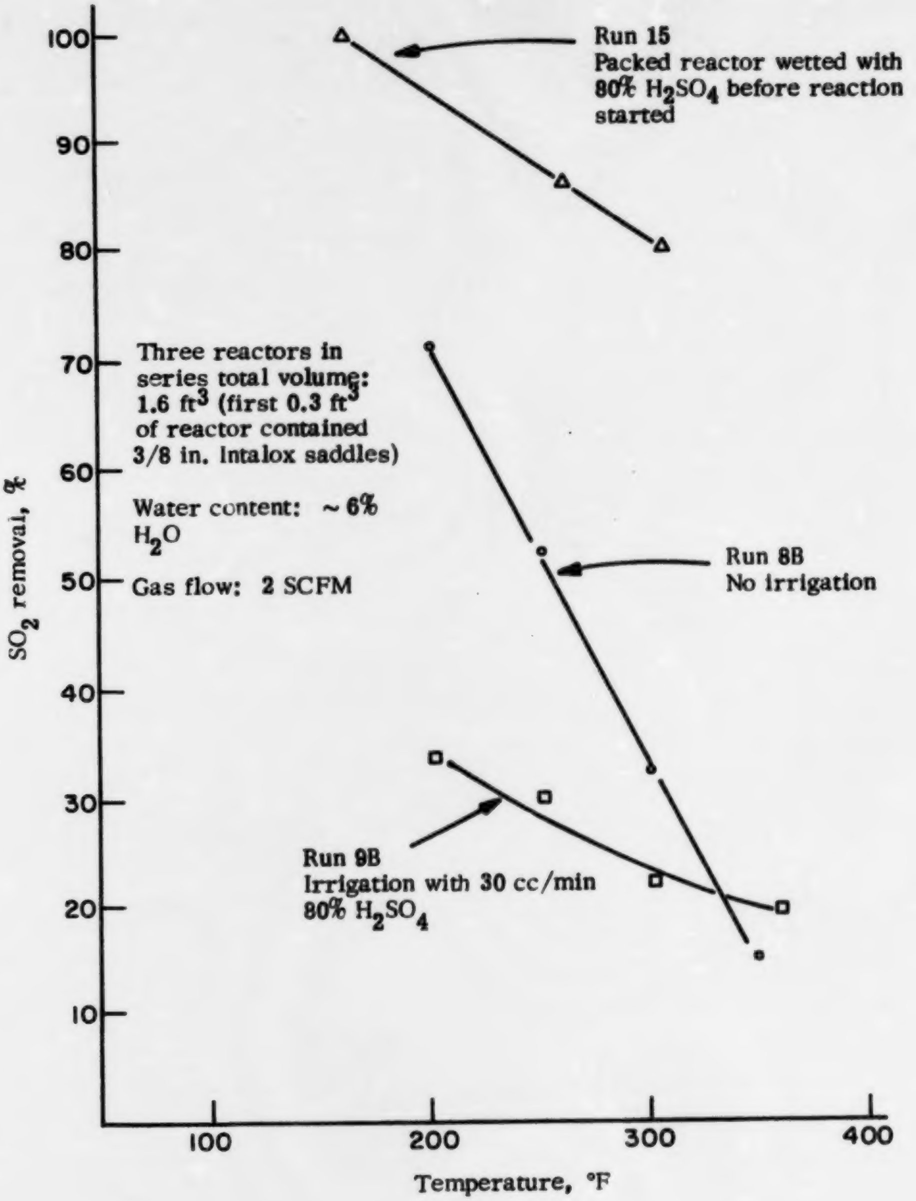


Fig. 11. Miniplant reactor experiment – SO_2 oxidation. Comparison of acid irrigation, wetted wall tests, and no irrigation

results shown in Fig. 12 make it clear that the 24 sec spent by the gas in the empty reactor sections contributed little or nothing to the reaction which was achieved in the 5 sec in the wetted saddles. This key test established that, under the existing conditions and gas concentrations of interest, the oxidation of SO_2 is achieved in the liquid phase.

These tests were followed by a series of experiments which attempted to optimize the liquid phase oxidation of SO_2. The first step was to pack all three reactor sections with 3/8-in. Intalox saddles and provide irrigation to the top of each column. This created a situation where reactors 1 and 3 were operated with the liquid and gas contacting each other in a cocurrent manner, while reactor 2 was in a countercurrent configuration (see Fig. 8). Several tests were run in which operating parameters were varied, including acid flow rate, acid concentration, and NO_x concentration (gas phase), but little improvement in reaction rate was achieved.

A typical reaction run is shown in Fig. 13. With elapsed time running from right to left, it can be seen that with no acid flowing it took about 1-1/2 hr for the system to reach steady state. During this time, the acid on the saddles was apparently building up in reactant concentration until a steady state condition was obtained. During this run, the effect of high oxygen concentrations in the flue gas was evaluated. This high oxygen content is the result of diluting the gas burner effluent gas with air in order to reduce the water content of the gas from about 20% to 6 to 8%. Instead of about 3% O_2, which is typical of coal burner flue gas, the simulated flue gas used in the current experimentation contains about 15% O_2. To determine the effect of this high oxygen level, an apparatus was constructed which permitted the dilution of the gas burner with nitrogen rather than air. Examination of Fig. 13 shows that the SO_2 content of the reactor effluent reached a steady state level of about 1050 ppm after approximately 1-1/2 hr. At this point, the diluent air was replaced with nitrogen and the experiment continued for another hour under these conditions. The nitrogen was then shut off and air returned to the dilution line. It is obvious that these changes had no effect at all on the oxidation rate of SO_2. It is therefore safe to say that, in general, the results of the experimentation were not affected by the presence of the high oxygen levels.

E. Instrumentation Considerations

During these last experiments, it was noticed that there was some apparent interference by the NO_2 on the SO_2 reading of the duPont UV Photometer. It was known that NO_2 absorbed to some degree at 302 mμ where the SO_2 was measured, but this was supposedly balanced out through the use of a reference beam which analyzed at a wavelength where SO_2 and NO_2 absorbed equally. In addition, there was a balancing potentiometer which permitted the interfering NO_2 to be zeroed out, so there should have been no apparent interference by NO_2 at the SO_2 absorbing wavelength. The problem was that, at the higher NO_2 levels used in some of the tests (up to about 15,000 ppm), this balance was not accounting for the interference.

Discussions with instrument people at duPont revealed that the balance control was effective at constant levels of NO_2 in the SO_2-bearing gas stream. If the NO_2 interference was balanced out at low NO_2 concentrations, there might well be very large levels of interference

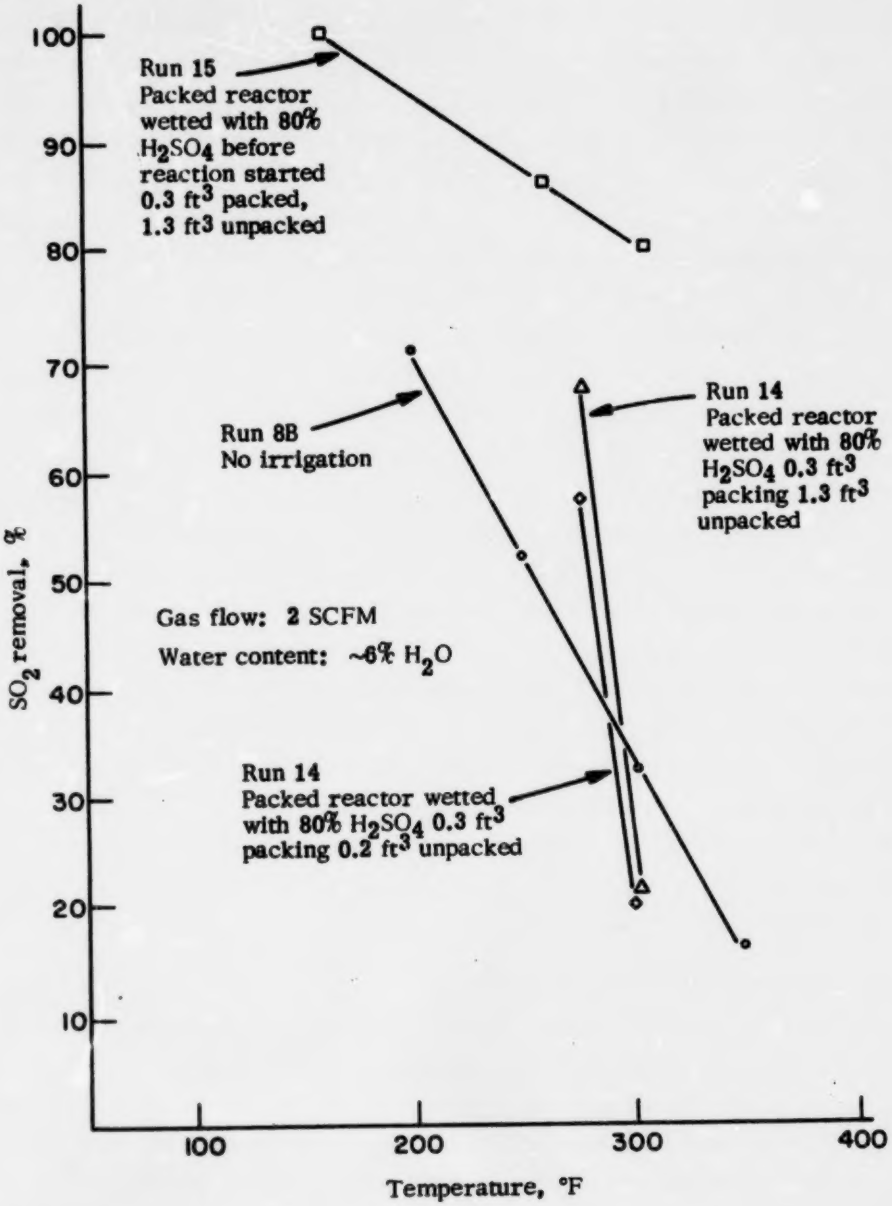


Fig. 12. Miniplant reactor experiments – SO_2 oxidation. Comparison of wetted-packing reactions with and without additional unpacked residence volume

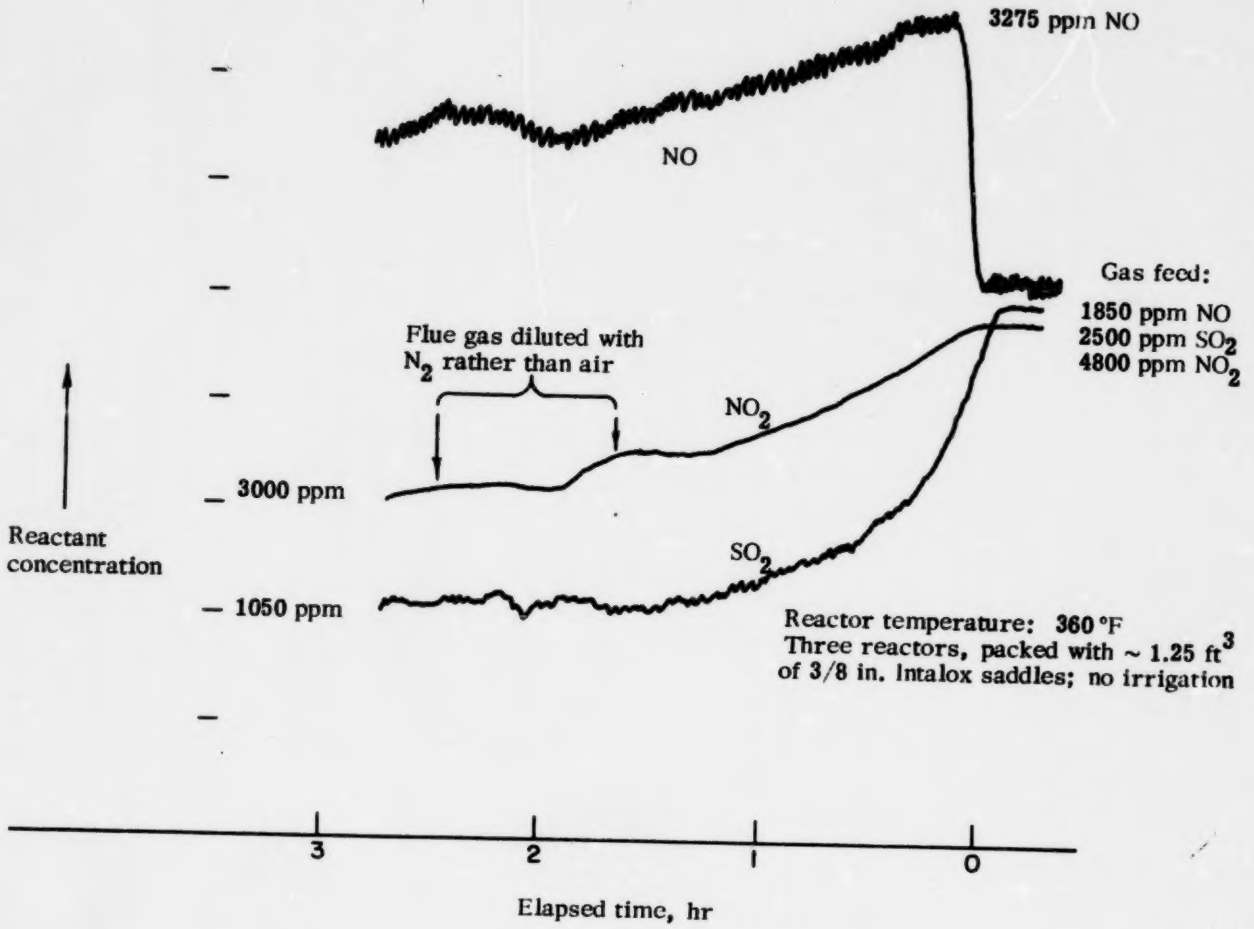


Fig. 13. Miniplant reactor experiment – SO_2 oxidation. Evaluation of low O_2 level in flue gas

at high concentrations. DuPont's recommendation was to balance the instrument at zero NO_2 concentration and run a calibration curve, giving SO_2 interference at various levels of NO_2. This was done, and the resulting interference curve is plotted in Fig. 14. The curve was obtained by reading SO_2 while feeding known concentrations of NO_2 to the UV cell. The interference level is approximately 30:1, which is about what was predicted by duPont. (This means that 30 ppm of NO_2 shows up as 1 ppm of SO_2.)

The high levels of NO_2 used in this stage of experimentation caused a difficulty in reading NO_2 concentrations above 1.5% (15,000 ppm) because of the saturation of the measuring photocell's ability to read low light levels. DuPont recommended a shorter UV cell to effect lower total absorbance in the cell. It was decided to replace the 15-in. cell with a 1.5-in. cell rather than put the two in series. By using a higher gain mode in the photometer amplifier, it was possible to use the shorter cell without loss in sensitivity at the gas concentrations of interest (up to 5000 ppm of SO_2 and 10,000 ppm of NO_2 full scale). The instrument could also be used to measure very low concentrations (500 ppm SO_2 and 1000 ppm NO_2 full scale), if desired. The advantage of this system is that it is possible to read NO_2 at both 10,000 ppm and 100,000 ppm full scale, thus permitting accurate analysis of the lower concentrations in the scrubber and reactor effluents and the higher concentrations in the stripper offgas.

The short cell was installed and the interference curve run again with the same levels of interference being observed. All further analysis indicated in this report was made with the short path UV cell unless otherwise noted. It was decided that, since the interference levels are quite low at the NO_2 concentrations being used throughout most of the experimentation, this phenomenon would be ignored unless the SO_2 concentrations were in the 0 to 500 ppm range. Reaction yields in future experiments will not take into account the NO_2 interference unless specifically noted.

F. Effect of Irrigation of Reactor with Nitrosylsulfuric Acid

It was apparent from the experimentation described above that the concentration of dissolved NO_x in the liquid phase was of considerable importance in determining the SO_2 oxidation rate. It was therefore decided to irrigate the reactor with $HNSO_5$ solutions in H_2SO_4 rather than H_2SO_4 alone.

Before discussing the runs where the reactor columns were irrigated with nitrosylsulfuric acid, it will be of value to examine two runs made with 80% sulfuric acid irrigation in order to gain some insight into the mechanism of the reaction. The operating data from these two 250 °F runs are shown in Figs. 15 and 16 and relate to Runs 27 and 28.

In Run 27, the three reactor columns are irrigated for some time with 80% sulfuric acid at the rather slow rate of about 30 cc/min for all three reactors (i.e., about 10 cc/min each). While the acid continued to drip into the reactors, the SO_2 input level was set at 3100 ppm (time zero). The SO_2 valve settings were fixed so that we could return to the same feed rate and the feed bottle was turned off.

For the next 1.5 hr, NO_x was fed to the columns as attempts were made to fix the desired NO and NO_2 feed rates. Acid continued to drip during this time. At the 1.75 hr mark of

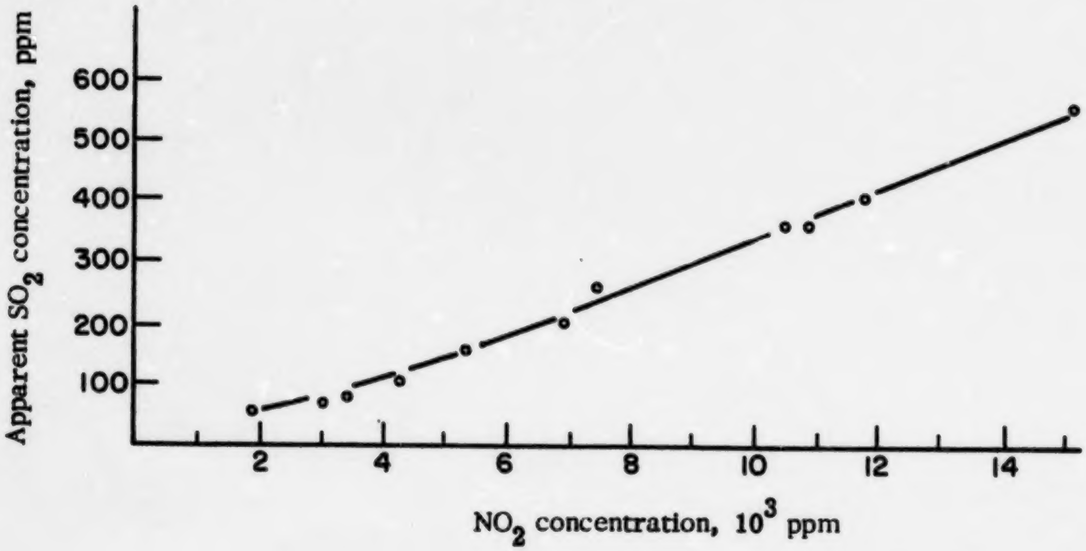


Fig. 14. NO_2 interference calibration curve

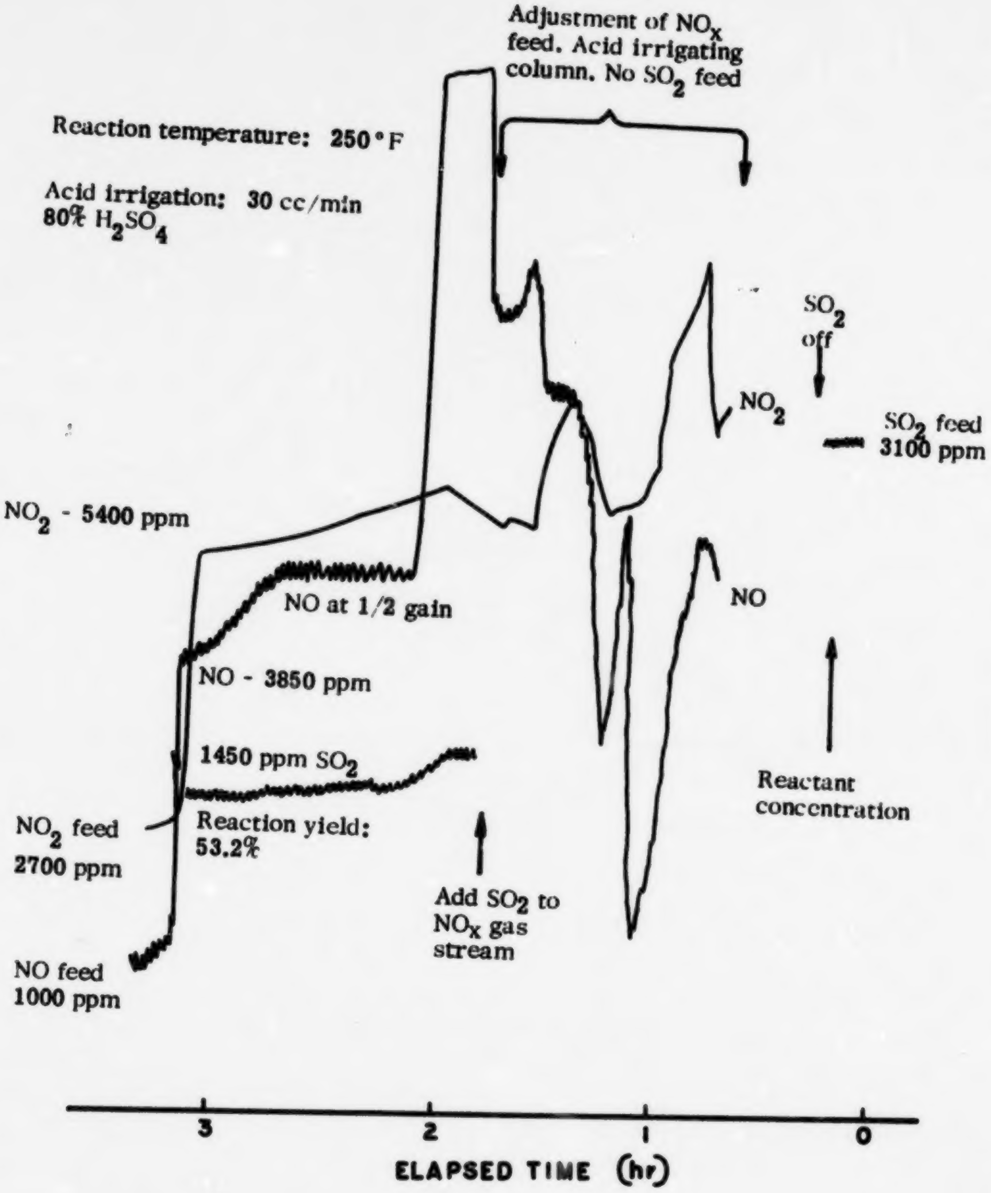


Fig. 15. Miniplant reactor experiment – SO$_2$ oxidation. Tracing of instrumentation recorder input (Run 27: evaluation of acid irrigation)

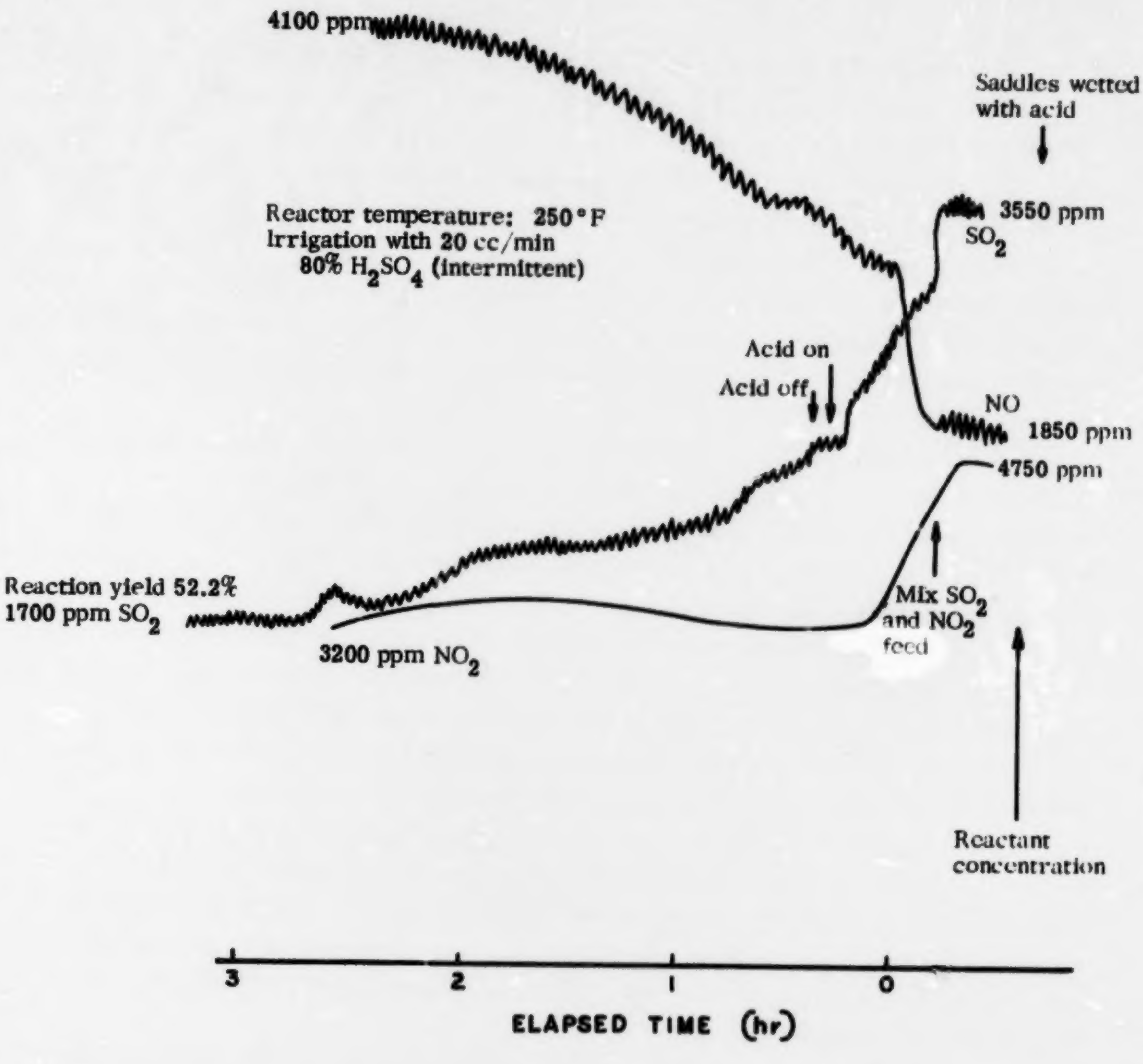


Fig. 16. Miniplant reactor experiment – SO_2 oxidation. Tracing of instrumentation recorder output (Run 28: evaluation of intermittent acid irrigation)

this run, the SO_2 was injected into the gas stream at the previous level and the gas concentrations were monitored for the next hours. The SO_2 level quickly leveled out and showed a reaction yield of 53.2%, based on the 3100 ppm input. When the SO_2 was introduced into the system, the NO level was monitored by cutting the gain in half, which accounts for the apparently low reading on the chart. The NO_2 level in the reactor effluent gas did not change much during the run.

At the end of the hour of testing, the SO_2 was turned off and the NO_x content measured at the reactor input side. It is highly significant that the NO_x feed rate was about 3700 ppm total while the reactor effluent gas during the run exhibited about 10,000 ppm of total NO_x.

The reasonable explanation for this behavior is that the acid on the column (which is not moving very rapidly at 10 cc/min for each column) absorbed a great deal of NO_x during the 1-1/2 hr of NO_x flow rate manipulation, and when the SO_2 was added, it rapidly reacted with the NO_x in solution and quickly reached a "steady state" reaction level. During this reaction period, the oxidation of the SO_2 caused the liberation of NO due to the reduction of the NO_2 values in the nitrose. The NO_x observed in the gas during the reaction far exceeded the input NO_x due to the reaction.

This hypothesis is further verified by the system shown in Fig. 16, Run 28. After the saddles were wetted with 80% sulfuric acid prior to time zero, the NO_x and SO_2 were introduced into the system almost simultaneously with no acid running. The SO_2 saw only gas phase NO_x and virtually pure sulfuric acid at the start of the run. With time, however, the NO_x was gradually absorbed into the acid on the saddles, and the SO_2 reacted with this NO_x at a gradually increasing rate. When the acid was added to the system on an intermittent basis (e.g., at the 20-min mark in the test), the reaction rate seemed to level out, but then continued to increase when the acid was allowed to sit on the column and absorb NO_x.

When the gas concentrations leveled out around the 3-hr mark, it could be seen that the effluent NO_x concentration in the gas phase was about the same as the input NO_x level (6600 ppm feed NO_x compared to 6300 ppm in the reactor effluent at steady state). This indicated that the NO_x was going into the liquid phase to enter into the reaction at the same rate at which it was leaving and a real steady state had been achieved. If Run 27 had been continued for several more hours, it is likely that the same steady state conditions would have been achieved. It is interesting to note that the reaction yield at steady state in Run 28 (52.5%) was about the same yield as in the earlier run (27).

Examination of these two runs makes it clear that it is not the NO_x in the gas phase that is important to the SO_2 reaction rate, but the amount of NO_x in solution. It seemed obvious at this point to irrigate with $HNSO_5$ solutions to introduce the NO_x with the acid rather than wait for it to be absorbed in the pure acid from the gas phase.

Two runs (29 and 30) were made to evaluate the effect of interacting flue gas with nitrose solutions rather than sulfuric acid solutions. The nitrose solution used contained 4.4% $HNSO_5$ in 70% sulfuric acid. The data from these runs are shown graphically in Fig. 17 (original data from all reactor experiments are in Appendix III) in comparison to data from acid-irrigated

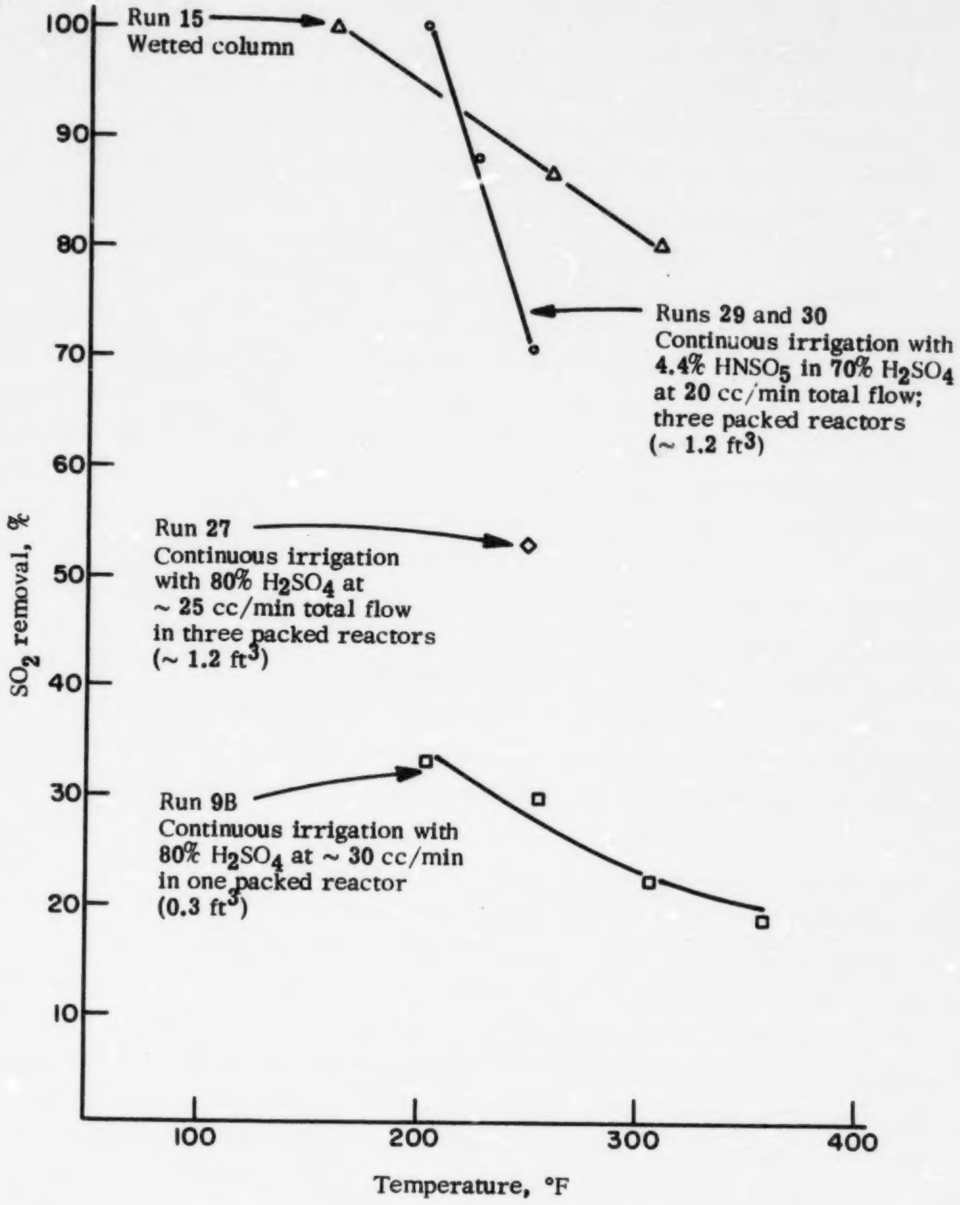


Fig. 17. Miniplant reactor experiment – SO_2 oxidation. Comparison of acid and nitrose irrigation

runs. It is clear that there is a definite advantage to irrigating with nitrose as considerably higher reaction yields are obtainable. Most of the data available with continuous acid irrigation were taken with the partially packed reactor (Run 9B in Fig. 17) and cannot be directly compared to the data from Runs 29 and 30, which were made using three completely packed reactors (top solid curve in Fig. 17); but the data from Run 27 can be used as a reference point since it, too, was made using all three packed reactor columns (single point in Fig. 17).

These data show a decided advantage to using nitrose solutions rather than dry reactors or pure acid irrigation, although comparison of the new data with earlier runs shows up an apparent inconsistency. If the data from Run 15 (Figs. 12 and 17) is compared with Runs 29 and 30, it would appear that continuous nitrose irrigation is not the only way to achieve high reaction yields. It should be recalled, however, that Run 15 was made under essentially nonsteady-state conditions. The single packed column was wetted with acid and then allowed to interact with the gas feed. The data points reproduced in Fig. 17 were the reaction yields under relatively constant conditions, but there is no doubt that after a considerable period of time the acid on the column would be removed and the efficiency of the reaction decreased. During the time that the data in Run 15 were taken, there must have been a buildup in the concentration of $HNSO_5$ in the acid remaining on the saddles, and this permitted the more rapid oxidation of SO_2.

Experiments were run to evaluate the effect on reaction rate of $HNSO_5$ concentration in the irrigation acid while maintaining constant H_2SO_4 concentration and constant reactor residence time. The results are shown in Figs. 18, 19, and 20. It is quite evident from the graphs that increasing the $HNSO_5$ concentration causes an increase in reaction rate.

The effect of varying the H_2SO_4 strength while maintaining all other conditions constant is shown in Fig. 21. As can be noted, decreasing the acid concentration causes an increase in reaction rate within the range of conditions studied.

Fig. 22 shows that the reaction yield increases with increasing reactor residence time, certainly a predictable result. In this figure, as in Figs. 18 through 21, the data clearly show that increasing the acid flow rate causes an increase in reaction rate. This has a bearing on the mechanism of the reaction which will be discussed later.

The data from Figs. 18 through 22 can be combined as in Fig. 23 to give some indication of the overall direction which must be taken to obtain high reaction yields. In this graph, acid flow rate was plotted against $HNSO_5$ concentration showing lines of constant reaction yield, constant acid concentration, and constant residence time. This method of presenting the data shows the trade-off between irrigation rate and $HNSO_5$ concentration to achieve the same reaction yield. It is highly significant that below a certain $HNSO_5$ concentration, the yield cannot be improved regardless of how much acid is used to irrigate the reactor. Conversely, below a certain irrigation rate, the yield cannot be improved even though the $HNSO_5$ concentration is greatly increased.

Fig. 24 points out that, although the irrigated column is highly effective in developing high reaction rates, the wetted columns also are quite effective in causing the oxidation and

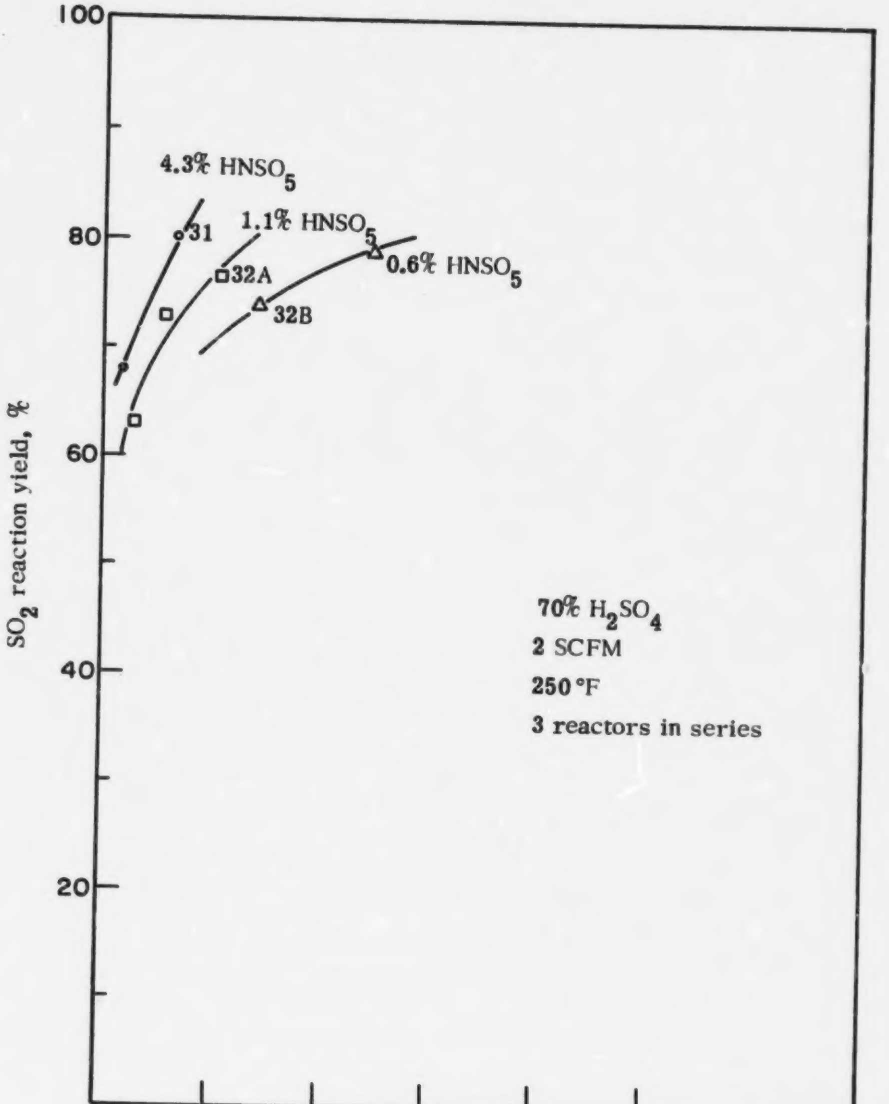


Fig. 18. Miniplant reactor experiment. Effect of HNSO$_5$ concentration on SO$_2$ removal yield

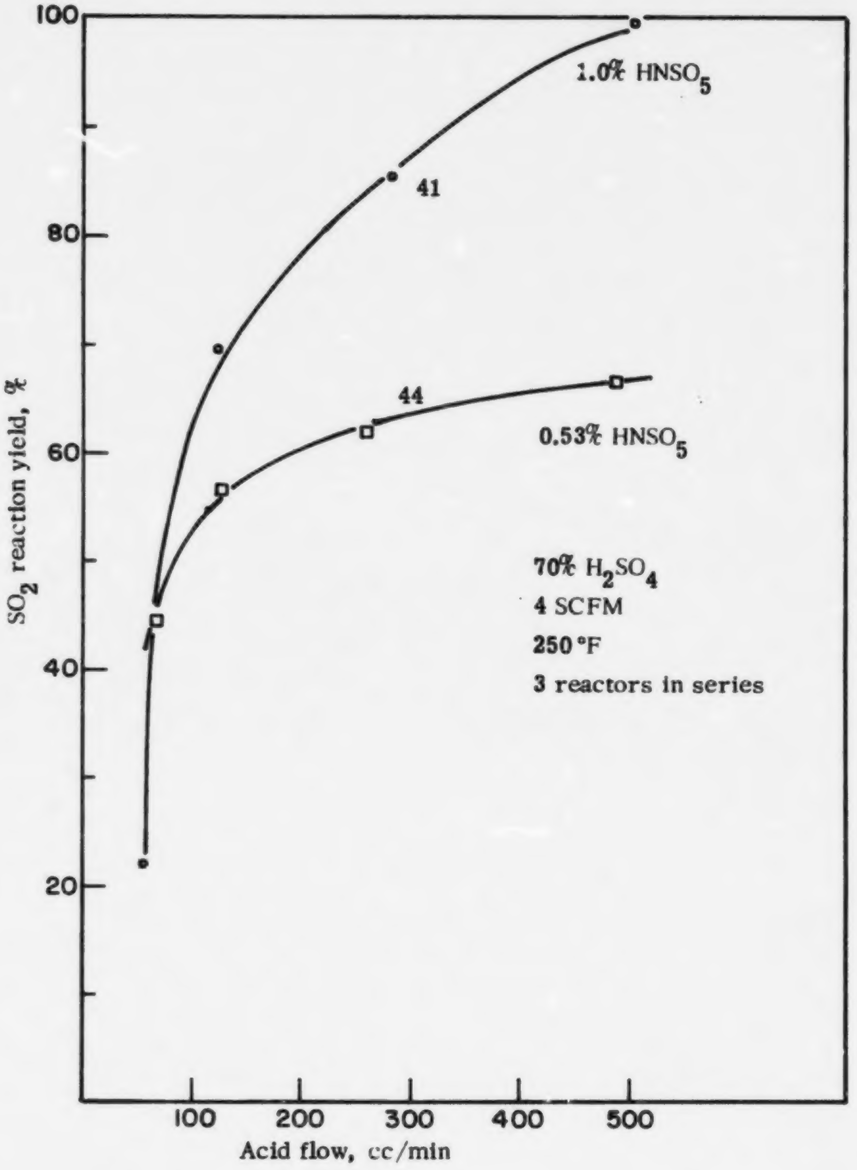


Fig. 19. Miniplant reactor experiment. Effect of HNSO$_2$ concentration on SO$_2$ removal yield

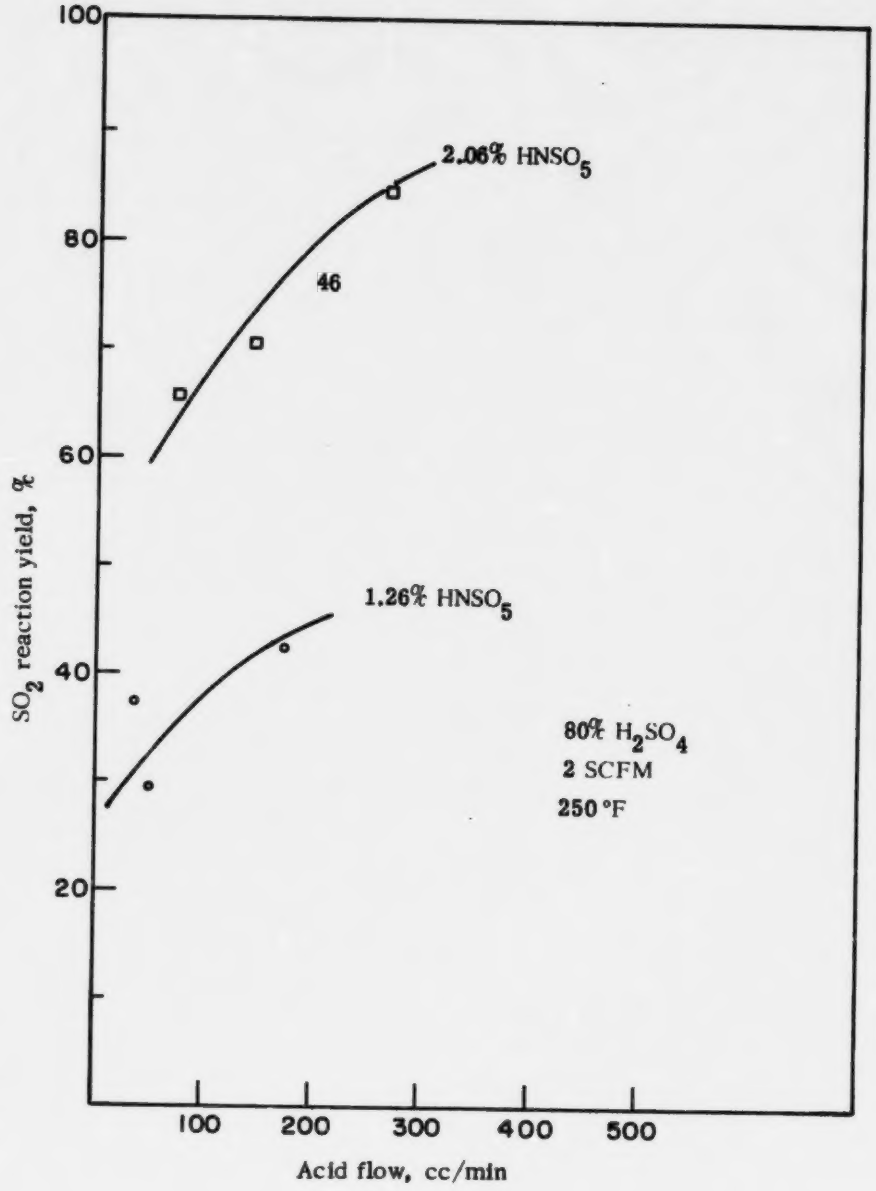


Fig. 20. Miniplant reactor experiment. Effect of HNSO$_2$ concentration on SO$_2$ removal yield

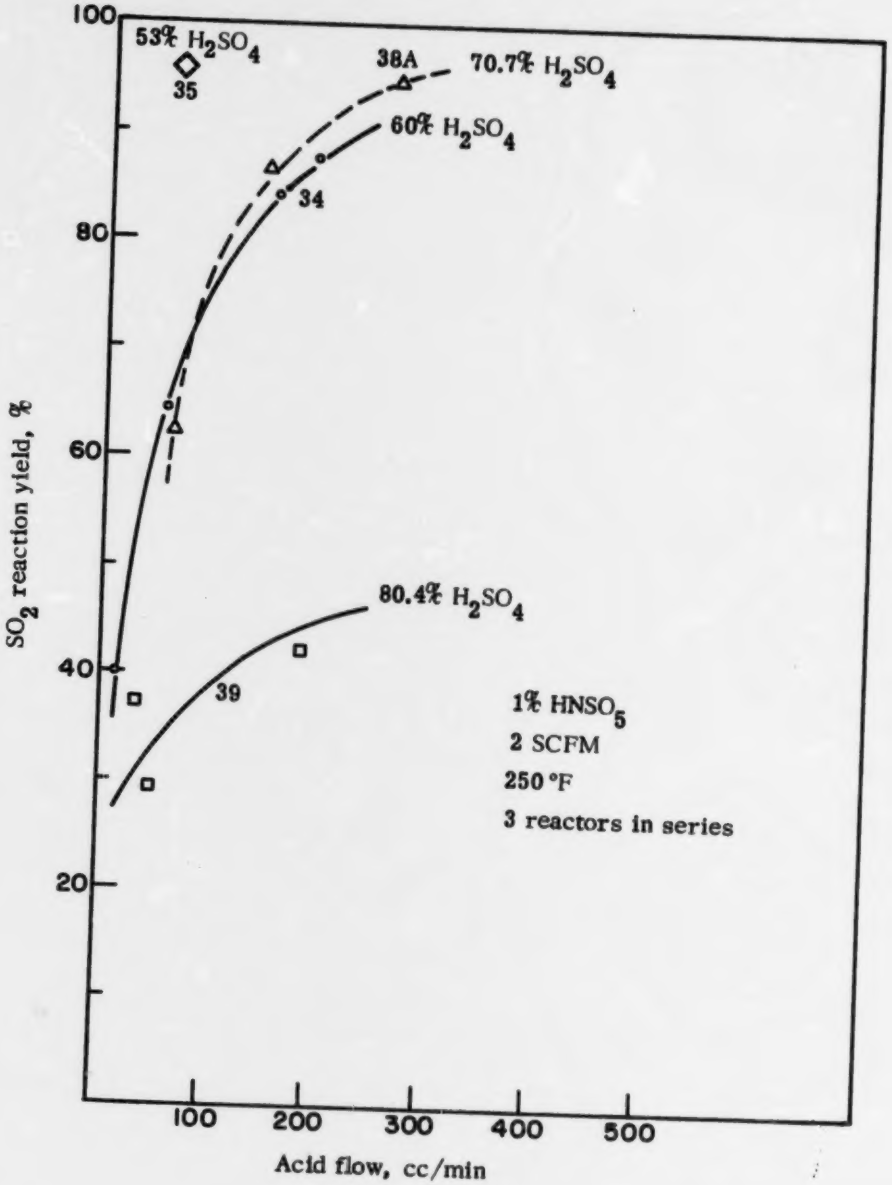


Fig. 21. Miniplant reactor experiment. Effect of H_2SO_4 concentration on SO_2 removal yield

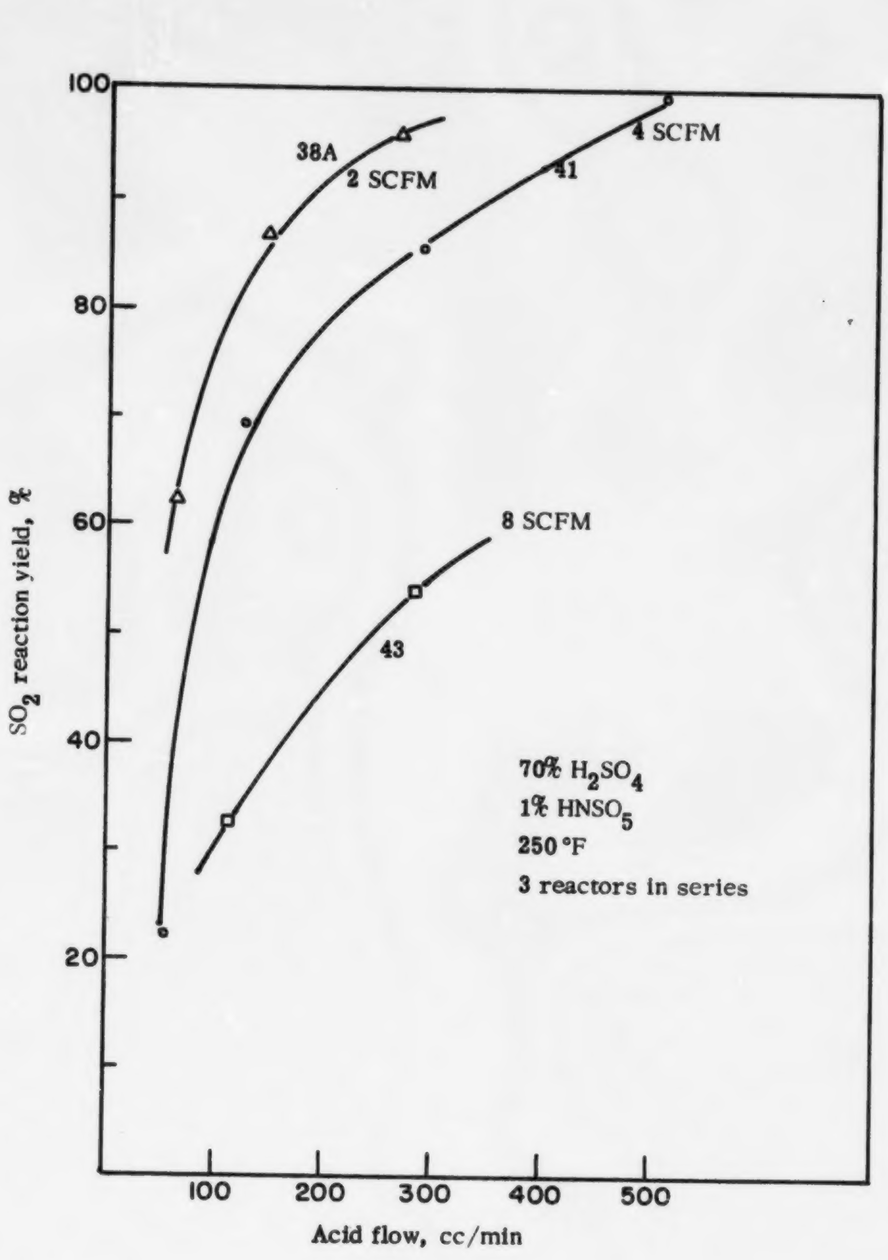


Fig. 22. Miniplant reactor experiment. Effect of residence time on SO_2 removal yield

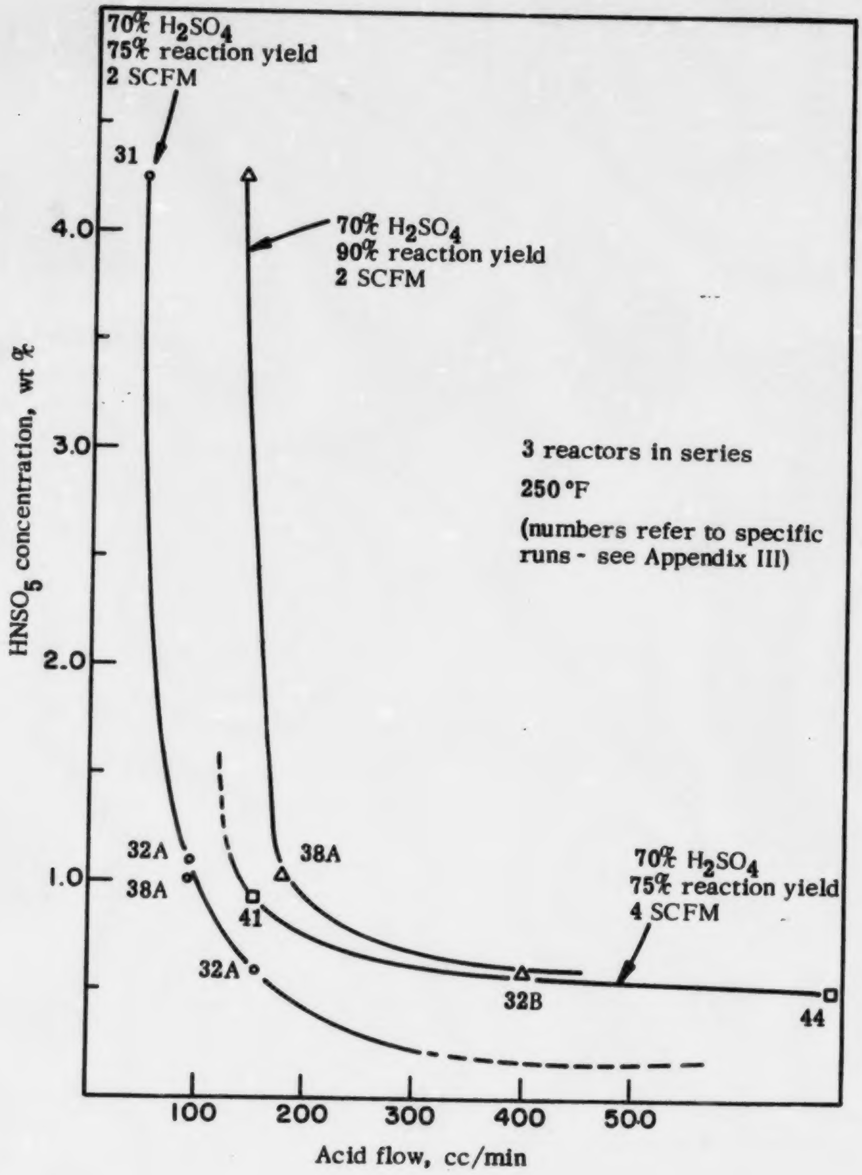


Fig. 23. Interpretation of miniplant reactor experimentation. Tradeoff between $HNSO_2$ concentration and irrigation flow rate in achieving a specific SO_2 reaction yield

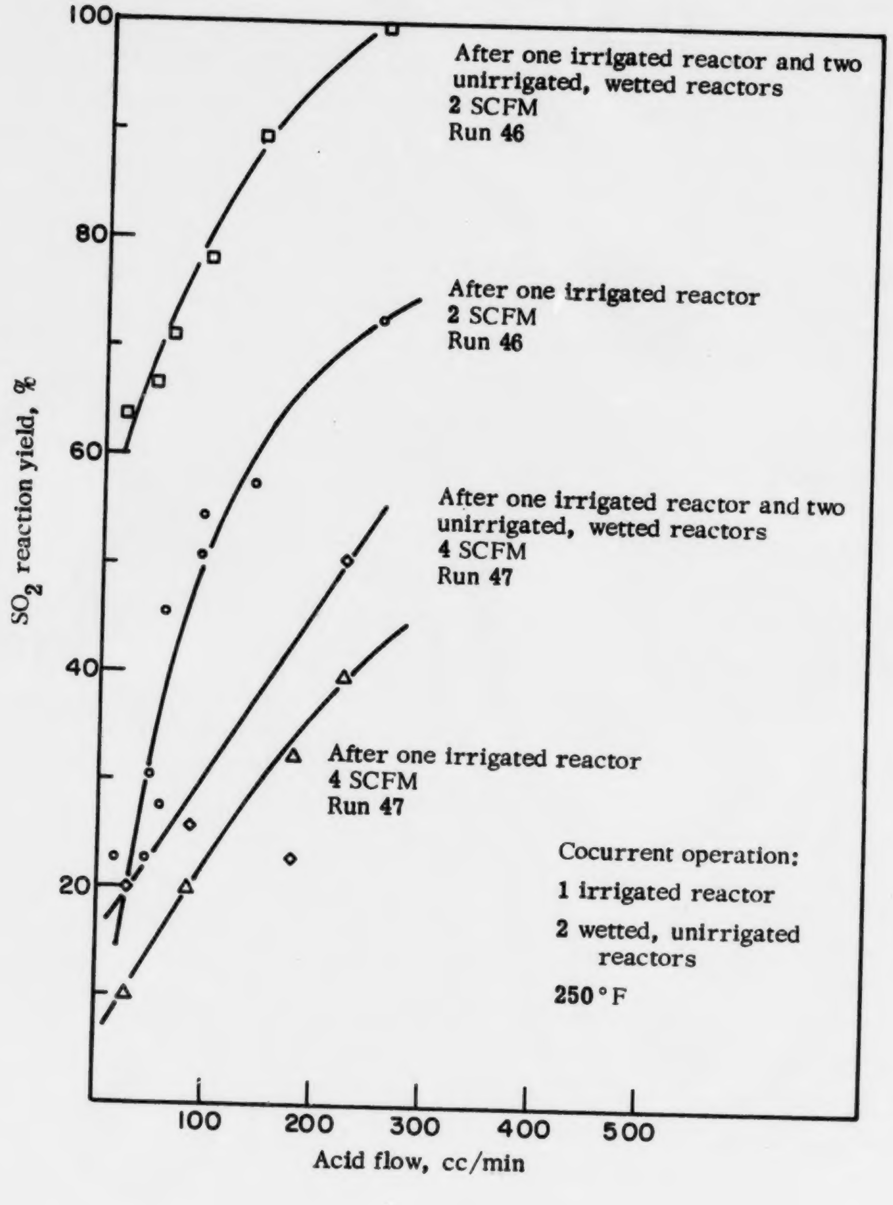


Fig. 24. Miniplant reactor experiments. Effect of irrigation and residence time on SO_2 removal yield

removal of SO_2. This verifies earlier data and has a bearing on the eventual operating mode of the reactor.

Four runs were made in one column only, the first two (Runs 46 and 47) being cocurrent operation while the other two (Runs 48 and 49) being countercurrent. The data on the cocurrent runs were taken from analyses made at the end of the first column, although the gases were passed through all three columns. The saddles in the second and third columns were still wetted with acid from previous runs and undoubtedly entered into the reaction. The gas effluent from the third column was also monitored. The countercurrent runs were made with one column only.

Fig. 25 shows the somewhat surprising result that there is essentially little difference between countercurrent and cocurrent operation. One might expect the countercurrent mode to be more effective in generating high reaction yields, but this is not the case. A possible explanation for this is the stripping of the $HNSO_5$ from the acid in the countercurrent mode before it gets a chance to react with the SO_2 entering the reactor from the other end. This might be offset by increasing the NO_x feed in the gas phase, which would tend to reduce the evolution of gas from the acid.

A series of liquid phase reactor experiments was run in the 15-ft packed miniplant reactor (see the data from Runs 52 through 62 in Appendix III). Runs 52 through 59 were run in a countercurrent mode while 60 through 62 utilized cocurrent operation. The significant result of this testing was that reaction yields in excess of 90% could be achieved in residence times under 15 sec. Realizing that additional testing would be eventually required to optimize the operation of the reactor at the pilot plant level, experimentation was halted at this point because it was clear that a reactor of practical size could be designed based on the information already learned.

Looking back at some of the earlier data (see final report to Contract No. CPA 70-59), it is possible to explain some of the anomalous results in terms of new knowledge. When the plant was operated such that there were long residence times in the sample lines, the reaction rate apparently increased with time in much the same manner as shown in Run 28 (Fig. 16). What must have been happening was the condensation of sulfuric acid in the sample lines followed by the absorption of NO_x in the condensate. The SO_2-bearing gas came through the sample lines and reacted with the nitrose on the walls the same way it reacts with nitrose on the saddles. Once steady state was reached, an apparently high reaction was achieved which was really occurring almost completely in the sample lines.

During the testing described above, these experimental artifacts were avoided. The lines were well heated and not easily contaminated (and were easily cleaned when there was condensation). The residence time in the sample lines was down to about 2 sec because of high sample flow rates and the low volume of the short UV analysis cell. The instrumentation behaved very well and data were both reproducible and reliable.

In looking over this data, it is clear that the nitrose irrigation concept represents a new approach to the problem of obtaining high SO_2 oxidation rates. There will be a discussion

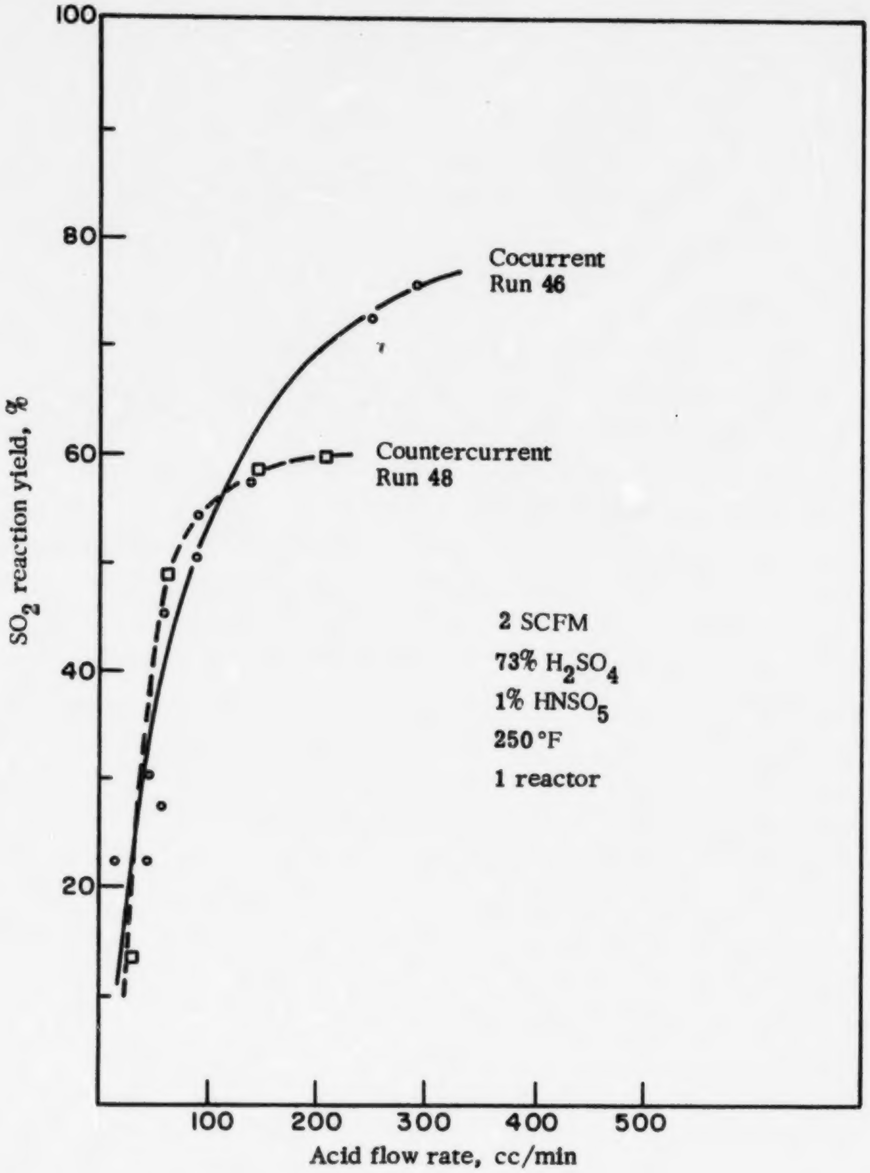


Fig. 25. Miniplant reactor experiments. Effect of countercurrent versus cocurrent reactor configuration

on reaction mechanisms and an analysis of a proposed flowsheet, including this new concept, later in this report. At this stage in the analysis of the reactor, it is safe to say that a more complete understanding of the reactor has been achieved, and it should be possible to continue to develop the process to the point where SO_2 can be removed from dilute gas streams in a practical manner.

G. SO_2 Oxidation Reaction Mechanisms

It was originally assumed that the overall chemical reaction occurring in the reactor was a gas phase oxidation:

$$NO_2 + SO_2 \rightarrow NO + SO_3$$

followed by, or simultaneously occurring with, hydration to form H_2SO_4. Experimentation during the early phases of this contract showed that this reaction does occur, but at too slow a rate to be economically feasible. However, subsequent testing showed that irrigation of the reactor with sulfuric acid or nitrose solutions gave considerably higher yields at equal residence times, and the most recent testing indicates 90% yields in less than 15 sec residence time. In order to more fully understand the process and thereby be able to further optimize the reactor stage, an in-depth analysis of the liquid phase reaction mechanism was initiated.

Two earlier studies, which are of direct relevance to the oxidation of SO_2 in the liquid phase by nitrogen oxide species in equilibrium with gas phase NO_x at 25 °C, are discussed here. The relevance of this work to our results at higher temperatures is clarified.

Berl, et al.[1] report the results of a study entitled, "The mechanism of the oxidation of SO_2 by oxygen in the presence of nitrosylsulfuric acid." The experiment involved the vigorous shaking together of 20 ml of 0.1 molar nitrosylsulfuric acid in sulfuric acid (20 to 80 wt %) with approximately 600 ml of a gas mixture consisting of 1/3 oxygen and 2/3 sulfur dioxide at approximately 25 °C. The rate of uptake of SO_2 was measured and found to be constant for any given sulfuric acid concentration. This rate was plotted versus sulfuric acid concentration and found to peak sharply at 57.5 wt % H_2SO_4. Further studies up to 90 °C indicated similar results. The rates of SO_2 conversion were much lower in the absence of a liquid phase.

Seel[2] reported the results of a study entitled, "The nitrous acid-nitrosyl ion equilibrium in aqueous sulfuric acid." A very careful ultraviolet spectroscopic study of nitrose solutions at 25 °C indicated that, whereas nitrous acid is the predominant nitrogen species at sulfuric acid concentrations less that 50 wt % H_2SO_4, nitrosyl ion (ionized nitrosylsulfuric acid) is the predominant nitrogen species at sulfuric acid concentrations greater than 70 wt % H_2SO_4. In the midrange, nitrous acid exists in equilibrium with hydrated nitrosyl ion, $H_2NO_2^+$, which is, of course, the same as protonated nitrous acid.

$$HNSO_5 \rightleftharpoons NO^+ + HSO_4^-$$

$$NO^+ + HSO_4^- + H_2O \rightleftharpoons H_2NO_2^+ + HSO_4^- \rightleftharpoons HNO_2 + H^+ + HSO_4^-$$

The concentrations of HNO_2 and $H_2NO_2^+$ are equal at 55 wt % H_2SO_4. At 59 wt % H_2SO_4, the conversion to $H_2NO_2^+$ is 90% complete. As the sulfuric acid concentration is further increased, the $H_2NO_2^+$ becomes less and less hydrated and thus becomes more correctly described at NO^+ (solvated by H_2SO_4).

Thus, at 57.5 wt % H_2SO_4:

1. Berl observed the highest rates of conversion of SO_2 to H_2SO_4
2. Seel observed that $H_2NO_2^+$ is the predominant nitrogen specie in nitrose solutions.

One may reasonably conclude that $H_2NO_2^+$ is the nitrogen specie in nitrose solutions which is responsible for the rapid conversion of SO_2 in the lead chamber process and in the Tyco SO_2 reactor.

In making a statement concerning the optimum nitrose concentrations for the Tyco SO_2 reactor, one must consider the effects of increasing the temperature from about 80 °F to the range of 200 to 300 °F. At 80 °F, 0.1 molar $HNSO_5$, and 64 wt % H_2SO_4, the partial pressure of nitrogen oxides is about 0.02 atm whereas at 200 and 300 °F, the corresponding partial pressures are 0.13 and 0.41 atm. Berl's experiments at room temperature were carried out at constant $HNSO_5$ concentration whereas our experiments at elevated temperatures are more closely approximated by conditions of constant vol % NO_x in the gas phase. It is entirely possible that, at our operating temperatures, we may obtain the highest concentration of $H_2NO_2^+$ (and thus the highest rate of oxidation of SO_2) at some concentration of sulfuric acid higher than 57.5 wt %.

We assume that the major portion of the SO_2 oxidation occurs in the liquid phase by reaction of dissolved SO_2 and nitrosyl ion, NO^+. The reaction is assumed to be irreversible, i.e., the reaction products do not inhibit the oxidation of SO_2. For our model we postulate the following processes and possible slow steps:

$$(SO_2)\ \text{gas} = (SO_2)\ \text{dissolved} \tag{1}$$

diffusion gradients in gas phase (1a)

diffusion gradients in liquid phase (1b)

$$NO + NO_2 + H_2SO_4 = 2NO^+ + 2HSO_4^- + H_2O \tag{2}$$

diffusion gradients in gas phase (2a)

diffusion gradients in liquid phase (2b)

$$SO_2 + NO^+ + H_2O = NO + H^+ + HSO_3 \tag{3}$$

$$HSO_3 + NO^+ + H_2O = NO + H_2SO_4 + H^+ \tag{4}$$

To make the situation mathematically tractable and to allow us to develop a physical model which closely approximates a packed column, we find it useful to introduce reasonable simplifications into the model. We will verify by direct calculation that our simplifications are reasonable.

The first simplification we propose is that we be able to ignore the diffusion gradient of SO_2 in the gas phase. A typical case which we may use for the purposes of our calculation is 3000 ppm SO_2 at 150 °C over 80 wt % H_2SO_4. We may obtain an extrapolated value for the solubility of SO_2 in 80 wt % H_2SO_4 at 150 °C using the data of Kuznetsov.[3] Using the data for 79 wt % H_2SO_4 and doing a least-squares fit of log (C_{SO_2}) versus 1000/T°K, one obtains statistical constants which, in turn, yield the value of 1.00 cc SO_2 dissolve per cc of sulfuric acid solution.

Jost gives estimates for diffusion coefficients.[4] We find that for gases,

$$D = \frac{f\eta}{\rho}$$

where f = 1 approximately, η = viscosity, and ρ = density. At STP, D values normally fall in the range of 0.1 to 1.0 cm^2/sec. We also find that D is proportional to T^n where n is in the range 1.5 to 2.0. Thus, at 150 °C we may estimate that D is approximately equal to 1 cm^2/sec. For liquids of the viscosity we are concerned with, D is approximately equal to $10^{-5} cm^2$/sec.

To calculate SO_2 flux we use Fick's first law,

$$J = -D\left(\frac{\partial c}{\partial x}\right) \quad .$$

In the gas phase we assume complete depletion of SO_2 and a diffusion layer thickness of 0.01 cm, which results in an SO_2 flux of 8.6×10^{-6} moles/(cm^2-sec). In the liquid phase we assume complete depletion of the SO_2 and the same diffusion layer thickness which, in turn, results in an SO_2 flux of 8.6×10^{-11} moles/(cm^2-sec). It is apparent that the limiting flux occurs in the liquid phase. Thus, even though the maximum flux of 8.6×10^{-11} moles/(cm^2-sec) might be occurring in the liquid phase, this is only 0.001% of the maximum flux in the gas phase.

The second simplification we propose is that we be able to ignore step 2 as a rate limiting step. The solubility of nitrosylsulfuric acid (0.1 moles/liter for the case given above) is much greater than the solubility of SO_2 (8.6×10^{-5} moles/liter for case given above) for the conditions prevailing in the reactor. There is, thus, a greater driving force for the formation of nitrosylsulfuric acid than for dissolved SO_2. We have confirmed experimentally that NO_x uptake is very rapid in the reactor. This allows us to disregard step 2 as being rate limiting. The third simplification we propose is that we eliminate reaction 4 as a rate limiting step. If either reaction 3 or 4 is rate limiting, one would expect that reaction 3 is slower because of the fact that one does not observe high concentrations of any reaction intermediate, such as HSO_3. We thus dismiss reaction 4 as being rate limiting.

Our simplified model now consists of the irreversible bimolecular reaction of one slightly soluble gas phase species with a dissolved, rather higher concentration liquid phase species. To evaluate this model for our system, a particular configuration was chosen which is compatible with the experimental work that was done. The system chosen was a packed column with countercurrent gas/liquid flow. The input SO_2 level is assumed to be 3000 ppm and the input NO_2 level to be 3000 ppm at a gas flow rate of 4 SCFM. The acid feed is assumed to be 80 wt % H_2SO_4 with 0.0623 M $HNSO_5$ (at 150°) present and a liquid flux of 0.17 gpm. The $HNSO_5$ concentration of 0.0623 M was chosen since it is the equilibrium concentration for 3000 ppm each of NO and NO_2 in the gas phase at 150 °C in 80 wt % sulfuric acid, as computed from the data of Berl and Saenger.[5]

The column utilized was 4 in. in inside diameter, packed with 1/4-in. Intalox saddles. Danckwerts[6] gives an effective area of 1.4 cm^2/cm^3 for superficial flow rates of 0.2 cm/sec on a 1/2-in. packing. From U.S. Stoneware data,[7] we see that a dry area difference of ~1.5-fold exists, and thus an effective area of 2.2 cm^2/cm^3 is expected and will be used in our calculations. (Note: In this region, the effective interfacial area is nearly a linear function of the superficial liquid flow rate (cm/sec so that we may easily refine our effective area estimate when we experimentally determine the superficial liquid flow rate).

The calculation we wish to make involves the solution of Eq. (5-64) of Danckwerts:[6]

$$E = \frac{\sqrt{\left(M\frac{E_i - E}{E_i - 1}\right)}}{\tanh \sqrt{\left(M\frac{E_i - E}{E_i - 1}\right)}}$$

where:

$$M = \frac{D_A K_2 B^\circ}{K_L^2}\ ; \quad E_i = \left(1 + \frac{D_B B^\circ}{Z D_A A^*}\right)\ ; \quad \overline{R} = K_L A^* D$$

as:

E = enhancement factor,

E_i = enhancement factor when rate of reaction is controlled by diffusion,

M = dimension less time quantity,

D_A = diffusivity of dissolved gas A (cm^2/sec),

D_B = diffusivity of reactant B (cm^2/sec),

k_2 = second order rate constant for reaction of A (ℓ /g mole sec),

k_L = liquid film mass transfer coefficient (cm/sec),

A^* = concentration of dissolved gas A at interface, in equilibrium with gas at interface (g moles/cm^3),

B° = concentration of B in bulk of liquid (g mole/cm^3),

Z = number of moles reacting with each mole of A, and

$\overline{R}$ = average rate of absorption over c[illegible]ct time t.

For the solutions of these equations, we need estimates of several parameters. The state-of-the-art[8] in estimating diffusion coefficients involves extrapolation of room temperature aqueous data by assuming

$$\frac{D\mu}{T} = \text{constant},$$

where D = diffusivity in cm^2/sec, μ = viscosity in centipoises, and T = temperature in °K. Typical diffusion coefficients for ions and slightly soluble gases are $1.5 \pm 10^{-5} cm^3/sec$ at 25 °C.[4] We may extrapolate the data of Schwab and Kolb[9] and obtain a value of 16.2 centipoise for the viscosity of 80% H_2SO_4 at 150 °C. The viscosity of water is taken as 1 centipoise at 25 °C. This leads to $D = 1.3 \pm 10^{-6} cm^2/sec$ for NO^+ or SO_2 in 80% H_2SO_4 at 150 °C.

As mentioned earlier, B° (concentration of NO^+) is taken as 0.0623 M. We assume A* to be the saturation value or the solubility of SO_2. From extrapolation of the data of Kuznetsov[3] to 150 °C and the assumption of the validity of Henry's Law, we obtain:

$$A^* = 1.16 \times 10^{-4} m$$

From Danckwerts, we obtain $k_L \sim 0.6 \times 10^{-2} cm/sec$ at 25 °C in water on 1/2-in. Intalox saddles. From Danckwerts[6] and also Gehlawat, et al.,[8] it is shown that k_L is proportional to D. This leads to $k_L = 1.16 \times 10^{-3} cm/sec$ at 150 °C in 80 wt % H_2SO_4. For k_2, the bimolecular reaction rate constant, we assume a value $\geq 10^8 \ell$ /mol-sec. (This is equivalent to saying that the bimolecular reaction is appreciably faster than the diffusion process.)

Using the parameter estimates obtained above, we calculate that E_i, the instantaneous enhancement factor, is equal to 269.5. Similarly, $M \leq 2.675 \times 10^4$. From Danckwerts[6] we confirm that $E = E_i$.

Finally, $\bar{R}$, the average rate of absorption of SO_2, is found to be $3.62 \times 10^{-8} mol/cm^2$-sec. Now that a value for $\bar{R}$ at the gas inlet to the reactor is determined, we may begin to calculate the conversion yield. The SO_2 flux is 2.528×10^{-4} mol/sec and the NO^+ flux is 8.028×10^{-4} mol/sec.

We choose to treat the problem by calculating the amount of time necessary to reduce the SO_2 level to 99.9% of its input level and then repeat this process until the desired conversion is attained. Before completing this calculation, we find the residence time for a typical column. For a 16-ft column, the residence time is 10.26 sec (Intalox saddles 75% void volume; void volume 3×10^4 cc; gas flux 2925 cc/sec at 150 °C).

The rate of SO_2 absorption is:

$$3.62 \times 10^{-8} \frac{\text{mol}}{\text{cc (total) - sec}}$$

for $2.2 cm^2$/cc (total) and for 6.482×10^{-8} mol SO_2/cc (total volume) in the gas phase. Note that because of the applicability of Henry's Law and the form of the Danckwerts rate equation, the rate of SO_2 absorption (mol/sec) is directly proportional to its concentration in the gas phase (mol/cc). Thus, the rate given above converts to:

$$1.23 \frac{\text{fraction } SO_2}{\text{sec}}$$

absorbed. This is the differential rate law for our column. To obtain the integrated degree of conversion, we need to sum the results for slight degrees of conversion as shown below.

To remove 0.1% of the SO_2 requires $\frac{0.001}{1.23} = 8.13 \times 10^{-4}$ sec ≡ τ sec. At the end of τ sec, 99.9% of the initial SO_2 is present. At the end of $n \cdot \tau$ sec, $100(0.999)^n$% of the initial SO_2 is present. We may calculate % conversion for various residence times. Such results are given in Table III.

We may continue our calculations and compute another table corresponding to conversion at 1/10 of the diffusion limited rate. This would be applicable if the bimolecular reaction was slower. From Danckwerts,[6] we see that the corresponding E factor of 26.95 occurs for M = 1600. We may calculate k_2 and determine conversions as shown in Table IV.

$$k_2 = \frac{M K_L^2}{D_A B^\circ} = 6.0 \times 10^7 \ \frac{cc}{g\ mol\ sec}$$

$$= 6.0 \times 10^4 \ \frac{\ell}{g\ mol\ sec}$$

Thus, it can be seen that 90% conversion of SO_2 will occur in the range of 2 to 18 sec residence time, and presumably much closer to the lower value. A reasonable series of assumptions of:

D_B 20% lower
B° 20% lower
D_A 20% higher
A^* Same
k_L 20% lower

provides the results shown in Table V of 90% conversion in 4.4 sec residence time and 99% conversion in 8.8 sec.

Table III. Degree of Conversion of SO_2 at 150 °C in 80% Sulfuric Acid for Various Residence Times with Diffusion of SO_2 Being the Rate Limiting Step (See Text for Full Details)

Residence Time (sec)	Column Length (ft)	% SO_2 Remaining	% SO_2 Conversion
8.13×10^{-4}	0.0012	99.9	0.10
8.17×10^{-3}	0.0128	99.0	1.00
0.0857	0.13	90.0	10.00
0.564	0.88	50.0	50.00
1.872	2.93	10.0	90.00
3.75	5.85	1.00	99.00
5.62	8.76	0.100	99.90
7.5	11.7	0.00988	99.99012
10.00	15.6	0.00045	99.99955

Table IV. Degree of Conversion of SO_2 at 150 °C in 80% Sulfuric Acid for Various Residence Time with Rate of Conversion Equal to 1/10 of the Diffusion Limited Rate (See Text for Full Details)

Residence Time (sec)	Column Length (ft)	% SO_2 Remaining	% SO_2 Conversion
0.00813	0.012	99.9	0.1
0.0817	0.13	99.0	1.0
0.857	1.3	90.0	10.0
5.64	8.8	50.0	50.0
15.39	24.0	15.07	84.9
18.72	29.3	10.0	90.0

Table V. Degree of Conversion of SO_2 at 150 °C in 80% Sulfuric Acid at Various Residence Times Using Modifying Assumptions Presented in Text (p. 59)

Residence Time (sec)	Column Length (ft)	% SO_2 Remaining	% SO_2 Conversion
0.00192	0.003	99.9	0.10
0.0193	0.03	99.0	1.00
0.202	0.31	90.0	10.00
1.35	2.1	50.00	50.00
4.42	6.9	10.00	90.00
8.84	13.8	1.00	99.00

VI. SCRUBBER EVALUATION

A. Initial Concept

As discussed in the introduction to this report, the purpose of the scrubber is to remove the oxides of nitrogen from the reacted stack gas, leaving the reactor stage after the oxidation of the SO_2. This is to be accomplished without removing water from the gas stream. The evaluation tests run during this contract were aimed at establishing two capabilities of the scrubbing system: absorption of NO_x at the high concentrations present after SO_2 oxidation by NO_2, and absorption of low concentrations of NO_x that would be present in raw flue gas. In this manner the Catalytic Chamber Process could be evaluated for combined NO_x/SO_2 removal as well as NO_x removal alone after the SO_2 was removed in a prior gas treatment step.

Prior experimentation, as discussed in the final report to Contract CPA 70-59, had established that a 4-in. column packed with 8.5 ft of 3/8-in. Intalox saddles could absorb about 65% of the NO_x from an equimolar mixture of 3000 ppm each of NO and NO_2. Extrapolation of this data indicated that a column about 30-ft high would absorb about 97% of the NO_x. Based on this work, the miniplant was used to evaluate the scrubber concept for absorption of NO_x from dilute and concentrated gas streams.

B. Experimental Procedures

The miniplant was set up as in Fig. 6 with two packed 4-in. diameter scrubber columns in series containing about 27 ft of 3/8-in. Intalox saddles. The three Teflon-coated stainless steel strippers were set up in parallel with the scrubber effluent acid being sent to the bank of strippers for denitration. In this manner the scrubber system could be operated continuously over a long period of time. It was decided that at the initial stages of scrubber evaluation, there was no need to run the reactor stage since the reactor work had already been completed (see Section V of this report). Therefore, the gas that was fed to the bottom of the large scrubber was composed of a simulated reactor off-gas containing about 6% water and approximately equimolar quantities of NO and NO_2 totaling 6000 to 7000 ppm NO_x for the first series of tests. The gas was passed through the large scrubber into the small scrubber and then to the stack. It was analyzed at three points: before and after the large scrubber and after the small scrubber. (At a later stage of experimentation, the gas was also analyzed half way up the large scrubber.)

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Nitrose-free sulfuric acid was fed to the top of the small scrubber with the effluent from this column being fed to the top of the large scrubber. Acid from the bottom of the large column was fed to the three strippers in parallel for denitration. The acid was analyzed at the bottom of each of the two scrubbers and as a composite at the bottom of the strippers. Air was fed to the strippers (at the bottom) and the effluent dumped to the stack after being analyzed for its NO_x content.

Temperatures in the system were controlled by externally mounted heating tapes and column mantles. The goal in temperature control was to feed the acid to each of the columns at the required temperature of column operation and use column heaters only to maintain the temperature. It was felt that it would be too difficult and inefficient to heat the acid while in the columns, especially in the 12-in. diameter strippers.

All temperatures were monitored on the two 24-point recorders while the gas analysis was performed on the duPont ultraviolet photometer and the Beckman infrared analyzer as in previous work. The acid was analyzed in batch tests using a hydrometer for H_2SO_4 concentration and potassium permanganate titration for $HNSO_5$ content. (See Appendix II for details of the $KMnO_4$ titration.)

C. Initial Experimentation — Parametric Study

In order to produce a useful amount of data in a short period of time, a parametric study was developed by Tyco and the Office of Air Programs (OAP) of EPA, which selectively varied certain key variables so as to obtain sufficient information in a series of twenty runs to develop a good feel for the scrubber operation. An outline of the study combined with a data sheet is shown in Fig. 26. This study was oriented around a combined NO_x/SO_2 removal process, and high levels of NO_x were used in the feed stream.

The first runs were made under the average conditions of the parametric study (see column 11 of Fig. 26). The raw data of these runs (nos. 67 and 68) are shown in Appendix IV as are all other scrubber/stripper experimental data. Run 69 was planned and then omitted. Runs 70, 70 (repeat), and 71 were run under the same conditions as the tests performed during the preceding Contract No. CPA 70-59, which showed approximately 65% scrubbing in an 8.5 ft column. Run 72 was a followup to 71 in an attempt to evaluate a higher L/G.

It is clear from examination of the data that the high scrubbing efficiencies expected by extension of earlier tests during the preceding contract were not achieved in any of these initial experiments. Where the data is most reliable, consistent readings show no better than 75 to 80% scrubbing instead of the anticipated 98%. (See Runs 67-72 in Appendix IV.) Confirmation of the analysis is obtained from two sources: NO_x material balance and consistent readings over a long period of time. The material balance errors of closure are shown in the table and are initially quite low (under 10%) in the first two runs, although later runs are more erratic. More will be said about this later. The consistency of the readings is shown by the subruns given by a letter designation in the table. These subruns show separate data points taken as the run progressed and, for the most part, imply a continuous operation of the plant at a given set of conditions.

	Units	Run Number Level 1	 Level 2	 Average																				
T_{NA}	°F	250	340	275	275	250	300	250	300	300	250	300	250	275	275	300	250	300	250	250	300	250	300	275
L_{NA}	16/hr-ft^2	915	3600	2290	2290	915	3600	915	3600	915	3600	915	3600	2290	2290	3600	915	3600	915	3600	915	3600	915	2290
L/G_{NA}	mole/mole	3.1	6.1	4.6	4.6	3.1	6.1	6.1	3.1	6.1	3.1	3.1	6.1	4.6	4.6	6.1	3.1	3.1	6.1	3.1	6.1	6.1	3.1	4.6
$GHSV_{HD}$	hr^{-1}(STP)	6.4	33.8	20.1	20.1	6.4	33.8	33.8	6.4	6.4	33.8	33.8	6.4	20.1	20.1	33.8	6.4	6.4	33.8	33.8	6.4	6.4	33.8	20.1
$[C_{NO_x}]_{F.G.}$	ppm	2000	10000	6000	6000	2000	2000	2000	2000	10000	10000	10000	10000	6000	6000	10000	10000	10000	10000	2000	2000	2000	2000	6000
$[C_{SO_2}]_{F.G.}$	ppm	0	500	250	250	0	0	500	500	0	0	500	500	250	250	500	500	0	0	500	500	0	0	250
Config.	-	Series(2)	Parallel(3)	S or P	S	S	S	S	S	S	S	S	S	S	P	P	P	P	P	P	P	P	P	P
	Units	Levels																						
$Q_{F.G.}$	SCFM	1.5, 3.0, 6.1, 12.0, (5.6)			5.6	3.0	6.1	1.5	12.0	1.5	12.0	3.0	6.1	5.6	5.6	6.1	3.0	12.0	1.5	12.0	1.5	6.1	3.0	5.6
Q_{Acid}	GPM	0.1, 0.4, (0.25)			0.25	0.1	0.4	0.1	0.4	0.1	0.4	0.1	0.4	0.25	0.25	0.4	0.1	0.4	0.1	0.4	0.1	0.4	0.1	0.25
Q_{Air}	SCFM	0.4, 0.6, 2.1, 3.1, (9.85, 1.25)			1.25	0.4	2.1	2.1	0.4	0.4	2.1	2.1	0.4	1.25	1.85	3.1	0.6	0.6	3.1	3.1	0.6	0.6	3.1	1.85
$LHSV_{HD}$	hr^{-1}	0.14, 0.22, 0.58, 0.86, (0.36, 0.54)			0.54	0.22	0.86	0.22	0.86	0.22	0.86	0.22	0.86	0.54	0.36	0.58	0.14	0.58	0.14	0.58	0.14	0.58	0.14	0.36
$\bar{G}_{NA}$	16/hr-ft^2	81, 160, 325, 640, (302)			302	160	325	81	640	81	640	160	325	302	302	325	160	640	81	640	81	325	160	302
$\bar{L}_{HD}$	16/hr-ft^2	37, 110, 148, 442, (92.5, 270)			270	110	442	110	442	110	442	110	442	270	92.5	148	37	198	37	148	37	148	37	92.5
$\bar{G}_{HD}$	16/hr-ft^2	0.27, 1.34, 1.41, 6.97, (4.14, 0.84)			0.84	0.27	1.41	1.41	0.27	0.27	1.41	1.41	0.27	0.84	4.14	6.95	1.34	1.34	6.75	95	1.34	1.34	6.95	4.14
L/G_{HD}	mole/mole	3.0, 4.4, 11.9, 15.4, 17.5, 23.0, 61.4, 92.1, (22.4, 34.2)			34.2	23.0	17.5	4.4	92.1	23.0	17.5	4.4	92.1	34.2	22.9	11.9	15.4	61.4	3.0	11.9	15.4	61.4	3.0	22.9
$[C_{NO_x}]_3^*$	% V	0.14-19.8, (2.99, 4.46)			4.46	1.48	0.57	0.14	5.95	3.77	5.65	1.42	15.1	4.46	2.99	1.75	4.96	19.8	0.49	0.77	0.51	2.01	0.19	2.99
$[HNSO_5]_3^*$	% W	0.03, 0.16, 0.40, 0.79, (0.32)			0.32	0.16	0.08	0.08	0.16	0.40	0.79	0.79	0.40	0.32	0.32	0.40	0.79	0.79	0.40	0.16	0.08	0.08	0.16	0.32

Tyco Mini-Plant Data

Date		-
T_{NA}		°F
T_{HD}		°F
$Q_{F.G.}$		SCFM
Q_{Acid}		GPM
Q_{Air}		SCFM
$[C_{HNSO_5}]$	1	% W
	2	"
	3	"
$[C_{H_2SO_4}]$	1	% W
	2	"
	3	"
$[C_{NO_2}]$	F.G.	ppm
	1	"
	2	"
	3	% V
$[C_{NO}]$	F.G.	ppm
	1	"
	2	"
	3	% V
$[C_{SO_2}]$	F.G.	ppm
	1	"
	2	"
	3	% V
$[C_{H_2O}]$	F.G.	% V
	1	"
	2	"
	3	"
$[C_{H_2O}]$	Air	% V

NOTES:

1. KEY: 1- Top of NO_x absorber; 2- Middle of NO_x absorber; 3- Top of $HNSO_5$ decomposer; F.G. - Flue gas.
2. $V_{Catalyst}$ = 3.72 ft^3 (series); 5.57 ft^3 (parallel).
3. A_{HD} = 0.70 ft^3 (series); 2.09 ft^3 (parallel).
4. Calculated, assuming that $[C_{HNSO_5}] = [C_{NO}] = [C_{NO_2}] = 0$

Fig. 26. Scrubber/stripper parametric study and data sheet.

Two major problems appeared which contributed to the difficulty of operation and, in part, to the low scrubbing efficiency. First of all, there was a great deal of difficulty in achieving continuous operation due to frequent pump failure. This was before the more reliable peristaltic pumps were installed. More pertinent to the scrubbing problem was the presence of a relatively high concentration of dissolved iron and chromium salts. The metal ions were clearly obvious in the acid as seen by the bright coloration of the acid while the fluid was hot and the presence of a light-colored precipitate throughout the system when the acid was cooled. Appendices V and VI of this report discussed in detail the source and influence of the dissolved metals on the efficiency of the scrubbing operation, but there did appear to be a connection between scrubbing efficiency and metal concentration in the acid.

Examination of the data for Runs 68 through 72 shows that as each run progressed, there was a decrease in scrubbing efficiency. This was due, in part, to the increase in temperature in the scrubbing columns, but even where the temperature was relatively constant there was a continued decrease in scrubbing. It is hard to evaluate the start of such an effect due to the way the system was brought up to operating conditions. Fresh acid was put in the system and the whole plant started up at room temperature. The acid was pumped around the entire loop through both the scrubbers and the strippers. When the plant was close to operating temperatures, the NO_x was introduced into the gas feed and the experimental data taken. By this time the acid had achieved the deep, bright green that was indicative of the relatively high concentration of chromium ion. Therefore, it was impossible from the data available to determine the scrubbing efficiency of uncontaminated acid under the desired operating conditions.

The source of the metal ions was not immediately apparent. Due to the failure of the Hastelloy B pumps, it was at first assumed that the corroding pumps were the source; but after it was determined that the metal ions were primarily chromium, this source was ruled out (there is no chromium in Hastelloy B). The only chromium in the system was in the Carpenter 20 of the piston pumps (which were not always in service during these runs and had not shown a tendency to corrode this severely in previous runs) and in the stainless steel of the several fittings used to connect the pumps into the glass pipe system. It was not until the end of the experimentation that the interior of the strippers was examined, and it could be seen that the Teflon coating had undergone massive failure and the chromium was indeed coming from the badly corroded stainless steel walls of these columns. (For a more complete discussion on corrosion of pumps and strippers, see Appendix VI.)

This problem with the coated strippers created a requirement for new stripper columns. New strippers were installed as shown in Fig. 6. The size and shape of the new columns was the same as before, so there was no change in operation.

After the new strippers were installed, Runs 74 through 81 were made, which indicated that under certain conditions it was possible to reduce the scrubber effluent to less than 150 ppm total NO_x (see Appendix IV, Run 74).

At this stage in the experimentation, the orientation of the program was shifted to low concentration removal of NO_x. A new parametric study was used to determine the run condition (see Table VI), with NO and NO_2 being introduced at 250, 500, and 1000 ppm each.

As indicated in Table VI, the stripper configuration was changed from three parallel columns (1 ft by 4 ft high) to two columns in series (1 ft by 8 ft high). A diagram of series stripper configuration is given in Fig. 27. An in-depth discussion of stripper performance is given in Section VIII of this report.

D. Mathematical Analysis of Experimental Scrubber Data

In this section, we present a mathematical treatment for the scrubber/stripper experiment. We also present a short discussion regarding scrubbing mechanisms. Actual data reduction follows at the end of this section and in Appendix VII.

We consider the experimental data to be a function of column height, column cross sectional area, and initial concentrations. Models of first and second order processes are developed. Equimolar NO and NO_2 are assumed for the beginning of each run when scrubbing is other than pure first order.

For first order scrubbing,

$$-\frac{dp_{NO}}{dt} = K_1 p_{NO} \qquad (1)$$

where:

P_{NO} = instantaneous concentration of NO in the bulk gas (atm),
t = time (sec), and
K = first order rate constant

$$\left(-\frac{dp_{NO_2}}{dt} = K_1 p_{NO_2}\right) . \qquad (2)$$

For second order scrubbing,

$$-\frac{dp_{NO}}{dt} = K_2 p_{NO} p_{NO_2} \quad \text{and} \qquad (3)$$

$$-\frac{dp_{NO_2}}{dt} = K_2 p_{NO} p_{NO_2} . \qquad (4)$$

For first and second order processes,

$$\text{flow rate}\left(\frac{ft^3}{sec}\right) = \frac{V}{t} = G, \qquad (5)$$

$$\text{volume } (ft^3) = V = Ah,$$

$$\text{time (sec)} = t = \frac{V}{t} = AhG^{-1}, \text{ and} \qquad (6)$$

$$dt = AG^{-1} dh \qquad (7)$$

Table VI. Parametric Study and Supplemental Work Plan

Run No.	Acid Flow GPM	Main Gas Flow SCFM	Stripper Gas Flow (Total) SCFM	L/G Moles/ Moles
82[p]	0.25	4.9	1.9	4.6
83[p]	0.40	11.7*	3.1	3.1*
84[p]	0.40	6.0	0.6	6.1
85[p]	0.10	1.5	3.1	6.1
86[p]	0.10	2.9	0.6	3.1
87[p]	0.25	4.9	1.9	4.6
88	0.20	2.9	3.1	6.2
89	0.40	2.9	3.1	12.4
90	0.10	6.0	3.1	1.5
91	0.10	11.2	3.1	0.8
92[s]	0.25	4.9	0.9	4.6
93[s]	0.10	2.9	1.6	3.1
94[s]	0.40	6.0	1.6	6.1
95[s]	0.40	11.7*	0.3	3.1*
96[s]	0.10	1.5	0.3	6.1
97[s]	0.25	4.9	0.9	4.6
98	0.25	11.7**	0.9	1.9**
99	0.25	4.9	0.9	4.6
100	0.62	4.9	0.9	11.4
101	0.25	4.9	0.9	4.6
102	0.25	4.9	0.9	4.6

Scrubber temperature: 275 °F
Stripper temperature: 290 °F

Flue gas composition:

H_2O	NO	NO_2
6%	250 ppm	250 ppm
	500 ppm	500 ppm
	1000 ppm	1000 ppm

---

[p] Parallel strippers parametric study.
[s] Series strippers parametric study.
* Actual gas flow was 8.8 SCFM, giving an L/G of 4.2 mole/mole.
** Actual gas flow was 8.8 SCFM, giving an L/G of 2.6 mole/mole.

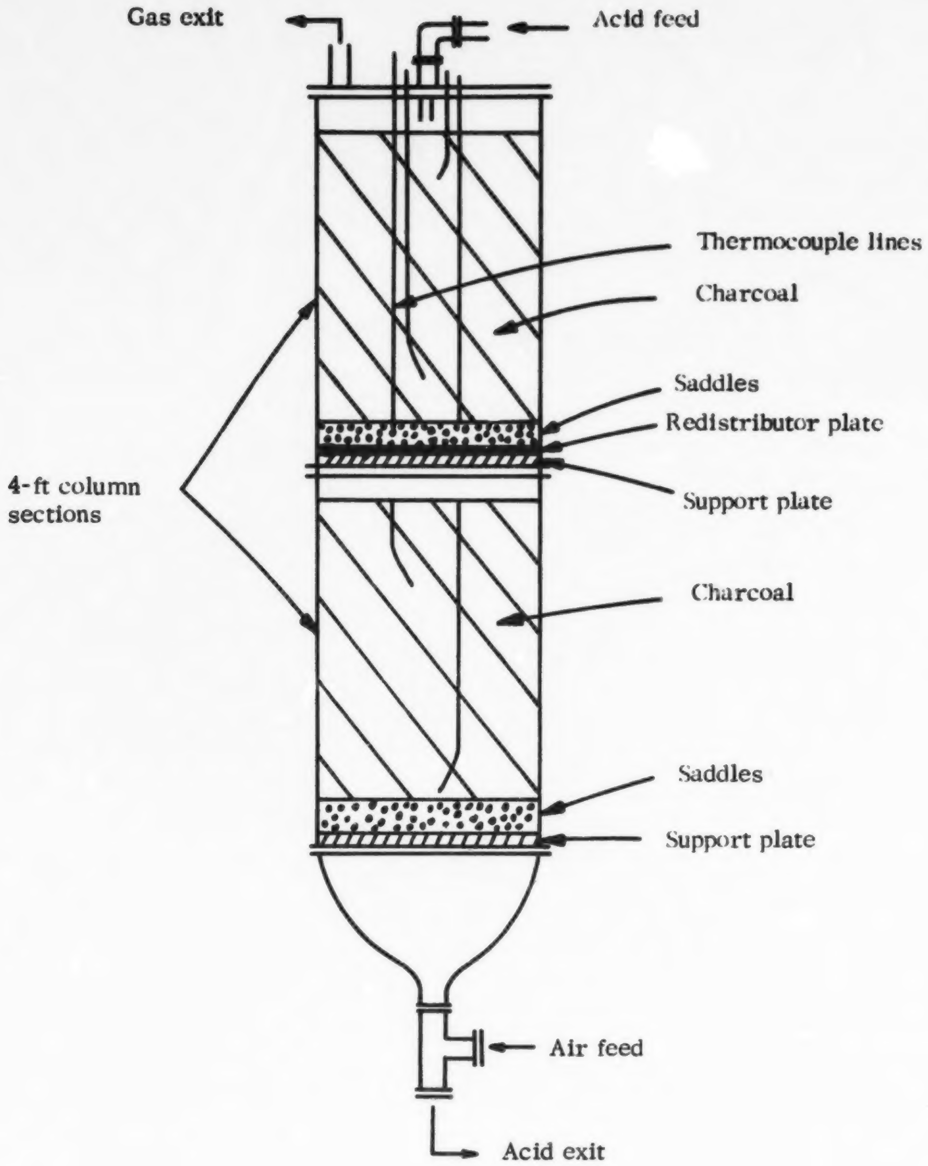
Gas exit
Acid feed
Thermocouple lines
Charcoal
Saddles
Redistributor plate
4-ft column sections
Support plate
Charcoal
Saddles
Support plate
Air feed
Acid exit

Fig. 27. Series stripper configuration.

for constants A and G.

Eqs. (1) through (4) become

$$-\ \frac{dp_{NO}}{dh} = \frac{AK_1p_{NO}}{G}\ , \tag{8}$$

$$-\ \frac{dp_{NO_2}}{dh} = \frac{AK_1p_{NO_2}}{G}\ , \tag{9}$$

$$-\ \frac{dp_{NO}}{dh} = \frac{AK_2p_{NO}p_{NO_2}}{G}\ , \text{ and} \tag{10}$$

$$-\ \frac{dp_{NO_2}}{dh} = \frac{AK_2p_{NO}p_{NO_2}}{G}\ . \tag{11}$$

For the second order process, assume that

$$p_{NO} = p_{NO_2} \tag{12}$$

and Eqs. (10) and (11) become

$$-\ dp_{NO} = \frac{AK_2p_{NO}^2}{G} \quad \text{and} \tag{13}$$

$$-\ dp_{NO_2} = \frac{AK_2p_{NO_2}^2}{G}\ . \tag{14}$$

Integrating the first order NO equation,

$$\int_{p_{NO}^0}^{p_{NO}^0} p_{NO}^{-1}\, dp_{NO} = -\ \frac{AK_1}{G}\int_0^H dh\ , \tag{15}$$

$$\ln_e\left(\frac{p_{NO}^0}{p_{NO}}\right) = K_1AHG^{-1}\ , \tag{16}$$

$$\log_{10}\left(\frac{p_{NO}^0}{p_{NO}}\right) = +K_1AHG^{-1}\log_{10}e\ . \tag{17}$$

Integrating the first order NO_2 equation,

$$\log_{10}\left(\frac{p_{NO_2}^0}{p_{NO_2}}\right) = +K_1AHG^{-1}\log_{10}e\ . \tag{18}$$

Integrating the second order NO equation,

$$\int_{p^0_{NO}}^{p_{NO}} p_{NO}^{-2}\, dp_{NO} = -\frac{AK_1}{G}\int_0^H dh \qquad \text{and} \tag{19}$$

$$\frac{1}{p^0_{NO}} - \frac{1}{p_{NO}} = -K_2AHG^{-1} . \tag{20}$$

Integrating the second order NO_2 equation,

$$\frac{1}{p^0_{NO_2}} - \frac{1}{p_{NO_2}} = -K_2AHG^{-1} . \tag{21}$$

Solving for expected P values:

First order - NO

$$p_{NO} = p^0_{NO} \exp(-K_1AHG^{-1}) . \tag{22}$$

First order - NO_2

$$p_{NO_2} = p^0_{NO_2} \exp(-K_1AHG^{-1}) . \tag{23}$$

Second order - NO

$$p_{NO} = \frac{p^0_{NO}}{1 + p^0_{NO}K_2AHG^{-1}} . \tag{24}$$

Second order - NO_2

$$p_{NO_2} = \frac{p^0_{NO_2}}{1 + p^0_{NO_2}K_2AHG^{-1}} . \tag{25}$$

Mechanistic tests that seem reasonable are easily devised. First, plot

$$\log_{10} \frac{p^0_{NO}}{p_{NO}}$$

versus $AHG^{-1}\log_{10}e$, and in the region where the plot is linear, NO is being removed by a first order process [cf. Eq. (17)]. The first order rate constant, K_1, is given by the slope. A similar plot may be made for NO_2. Second, plot

$$\frac{1}{p^0_{NO}} - \frac{1}{p_{NO}}$$

versus $(-AHG^{-1})$ and in the region where the plot is linear NO is being removed by a second order process [cf. Eq. (20)]. A similar plot may be made for NO_2.

Note that in the foregoing tests the intention is to plot all of the data on four plots:

1. First order NO plot.
2. First order NO_2 plot.
3. Second order NO plot.
4. Second order NO_2 plot.

Putting all of the runs on only four plots will have the effect of averaging the data. By visual inspection one may determine whether or not the data falls into any significant groups. When this has been ascertained, one may perform meaningful, weighted, least-squares fits of selected data groups to obtain first- and second-order rate constants applicable to various scrubbing conditions.

When rate constants have been calculated, one may calculate percentage scrubbing for various scrubbing conditions and column geometries on the basis of first- or second-order constants [Eqs. (22) through (25)]. For a somewhat more precise treatment, one may derive rate equations for simultaneous first- and second-order processes.

If NO were removed by second-order processes only and NO_2 is both first- and second-order processes, we would write:

$$- \frac{dp_{NO}}{dh} = \frac{AK_2 p_{NO} p_{NO_2}}{G} , \tag{8}$$

and

$$- \frac{dp_{NO_2}}{dh} = \frac{AK_1 p_{NO_2}}{G} + \frac{AK_2 p_{NO} p_{NO_2}}{G} \tag{26}$$

We may solve these equations only if we can obtain an expression relating p_{NO} and p_{NO_2}. Experimental observations tend to indicate that except at very low NO levels, we may validly use the approximation:

$$p_{NO} = p_{NO_2} \; . \tag{12}$$

For NO, we obtain:

$$p_{NO} = p^0_{NO} \exp(-K_1 AHG^{-1}) \; . \tag{22}$$

For NO_2,

$$\int_{p^0_{NO_2}}^{p_{NO_2}} \frac{dp_{NO_2}}{K_1 p_{NO_2} + K_2 p^2_{NO_2}} = -AG^{-1} \int_0^H dh \; . \tag{27}$$

From the general integral solution:

$$\int \frac{dx}{x(a+bx)} = -\frac{1}{a} \ln_e \left(\frac{a+bx}{x}\right) , \tag{28}$$

we obtain

$$\int_{p^0_{NO_2}}^{p_{NO_2}} \frac{dp_{NO_2}}{K_1 p_{NO_2} + K_2 p^2_{NO_2}} = \frac{1}{K_1} \ln \left\{ \frac{p_{NO_2}\left(K_1 + K_2 p^0_{NO_2}\right)}{p^0_{NO_2}\left(K_1 + K_2 p_{NO_2}\right)} \right\} . \tag{29}$$

Then,

$$\frac{p_{NO_2}\left(K_1 + K_2 p^0_{NO_2}\right)}{p^0_{NO_2}\left(K_1 + K_2 p_{NO_2}\right)} = \exp\left(-K_1 AHG^{-1}\right) , \tag{30}$$

and finally,

$$p_{NO_2} = \frac{K_1 p^0_{NO_2} \exp\left(-K_1 AHG^{-1}\right)}{K_1 + K_2 p^0_{NO_2} \left[1 - \exp\left(-K_1 AHG^{-1}\right)\right]} . \tag{31}$$

We may see if Eq. (31) reduces to Eqs. (23) or (25) as K_2 or K_1 approach zero, respectively. As K_2 approaches zero, Eq. (31) becomes:

$$p_{NO_2} = p^0_{NO_2} \exp\left(-K_1 AHG^{-1}\right) . \tag{23}$$

At small values of K_1, we may approximate:

$$e^{-x} = 1 - x , \tag{32}$$

and Eq. (31) becomes

$$p_{NO_2} = \frac{p^0_{NO_2} - K_1 p^0_{NO_2} AHG^{-1}}{1 + K_2 p^0_{NO_2} AHG^{-1}} . \tag{33}$$

And, as K_1 approaches zero, this becomes:

$$p_{NO_2} = \frac{p^0_{NO_2}}{1 + p^0_{NO_2} K_2 AHG^{-1}} . \tag{25}$$

Thus, the more general equation (Eq. 31) reduces to the simpler equations (Eqs. 23 and 25) in the limiting cases.

We may now calculate percentage scrubbing for various scrubbing conditions and geometries, using Eqs. (22) and (31). The only restrictions that apply are that p_{NO} should not be significantly lower than p_{NO_2} if Eq. (31) is to hold exactly. The necessary calculations may be easily performed on a computer.

When we perform the calculations we should be aware that we can make reasonable guesses at the "chemistry-of-the-scrubbing-process" on the basis of our data treatment. Our preliminary guess regarding the rate limiting step in the second order process is that it involves gas phase combination of NO and NO_2 to form gaseous N_2O_3 which then rapidly dissolves in the acid. If this view is correct, the K_2 values should be reasonably constant for any given temperature and reasonably independent of gas flow rate, liquid flow rate, column length, and column cross-sectional area. Our preliminary guess regarding the rate limiting step in the first order process is that it involves dissolution and/or liquid phase disproportionation of NO_2. If this view is correct, the K_1 values should be dependent on temperature, gas flow rate, and liquid flow rate.

E. Analysis of Scrubber/Stripper Data

Both Tyco scrubbing data for 80% sulfuric acid and OAP scrubbing data[10] for aqueous base solutions were analyzed. Not all of the Tyco data was utilized. Experimental scatter was the primary criterion for excluding data. Only total column scrubbing data were plotted and discussed in detail; the 10-ft and 19-ft data were not used.

Before commencing the data reduction, it is possible to obtain an estimate of the degree of reproducibility obtainable with the Tyco equipment. One may compare the percent removal for the centerpoint runs which represent the average conditions in the parametric study in Table V; data for these runs: 82, 87, 92, and 97, are given in Appendix IV). The scrubbing efficiencies were 63.2, 72.8, 88.1, and 72.6% NO_x removal. The difference in scrubbing efficiencies is 9.6% for Runs 82 and 87 and 5.5% for Runs 92 and 97. The average difference in scrubbing efficiencies for the series and parallel stripper configurations is 12.3%. Since the acid from the stripper was quite well denitrated and would not be expected to influence the results, we must view these differences in scrubbing efficiency as an indication that experimental scatter is high. To partially overcome these difficulties, we used averaged data for the following analysis presented in this section.

One may also obtain a good estimate of the scrubber NO_x removal imbalance, i.e., whether or not NO and NO_2 were scrubbed in an equimolar ratio. For this purpose we consult Table VII-1 in Appendix VII which is a summary sheet of the Tyco scrubbing data. The first column gives the run number and the second column gives the flow rate in SCFM. The next four columns give inlet and outlet concentrations in ppm. The seventh and eighth columns give the amount of material scrubbed from the gas stream (in ppm) and the last column gives the difference of the values in the seventh and eighth columns (in % error). Thus, the NO_x error value of 20 listed for Run 82AB indicates that 20 ppm more NO than NO_2 was scrubbed. (The analogous OAP data are presented in Table VII-4 in Appendix VII.) In an attempt to determine the source of this NO_x error, one may determine average values of the NO error for certain groupings of the data. This data is presented in Table VII-2 in Appendix VII. For the six groupings listed, the values for the average NO_x error range from −01 ppm to +32 ppm. Though the standard deviations in these average values are high (between 140 and 300 ppm), the value for the average NO_x error is 120 ppm more positive for the 80 series than for the 90 series (see data tables in Appendices IV and VII for details). This might be indicative of an analytical error, perhaps caused by a change in the experimental setup or due to a time dependent factor, such as "drift," in the analytical equipment. Also, there is definitely a trend toward more positive values of the average NO_x errors as the input NO_x levels to the scrubber increase. This might reflect concentration dependent analytical errors or it might reflect the air oxidation of NO to NO_2.

In the foregoing paragraphs, we have discussed sources of variation in the NO_x analyses. The deviations noted are of the order of 100 ppm. The averages of the absolute values of the NO_x errors are 60, 90, and 140 ppm for the 250, 500, and 1000 ppm each of NO and NO_2 input levels, respectively. This amounts to an error which is 20 to 100% of the output NO_x levels. Since the calculation of rate constant values is sensitive to rather small deviations in the output levels, one may expect that the rate constant values we obtain will show wide variance. Such is the case.

The Tyco data analyzed in this section is presented in Table VII-3 in Appendix VII. The OAP data is presented in Table VII-4 in Appendix VII. Rate constants were calculated with the aid of the computer programs given in Table VII-5 and Table VII-6 in Appendix VII. The resulting rate constants are given in Table VII-7, Table VII-8 in Appendix VII, and Figs. 28 through 31. Only the Tyco results for the total column height of 26-1/2 ft are discussed in this section.

Due to the high variance observed with these calculations, one may not draw firm conclusions solely on the basis of the numerical values presented here. Figs. 28 through 31 indicate that the scrubbing reactions are neither pure first order or pure second order reactions. The upward slope of the K1 plots coupled with the downward slope of the K2 plots is indicative of rate limiting steps which are intermediate between first and second order. We postulate, but cannot prove (with the data presented here), that the observed results are a result of a bimolecular reaction with some mass transfer control. If sufficient data on basic column parameters were available, we might be able to apply calculations similar to those given in the section on the reactor mechanism.

The most conclusive evidence that we have regarding the scrubbing mechanism comes from the wide range of experimental conditions covered by the Tyco and OAP work. Within experimental error, essentially the same scrubbing rate constant values were observed for 80 wt % sulfuric acid, water, alkaline earth hydroxide slurries, and concentrated sodium hydroxide solutions. Nitrosyl ion is the stable nitrogen specie expected to be formed in the scrubber under strongly acid conditions, such as 80 wt % H_2SO_4. Nitrite ion is the stable

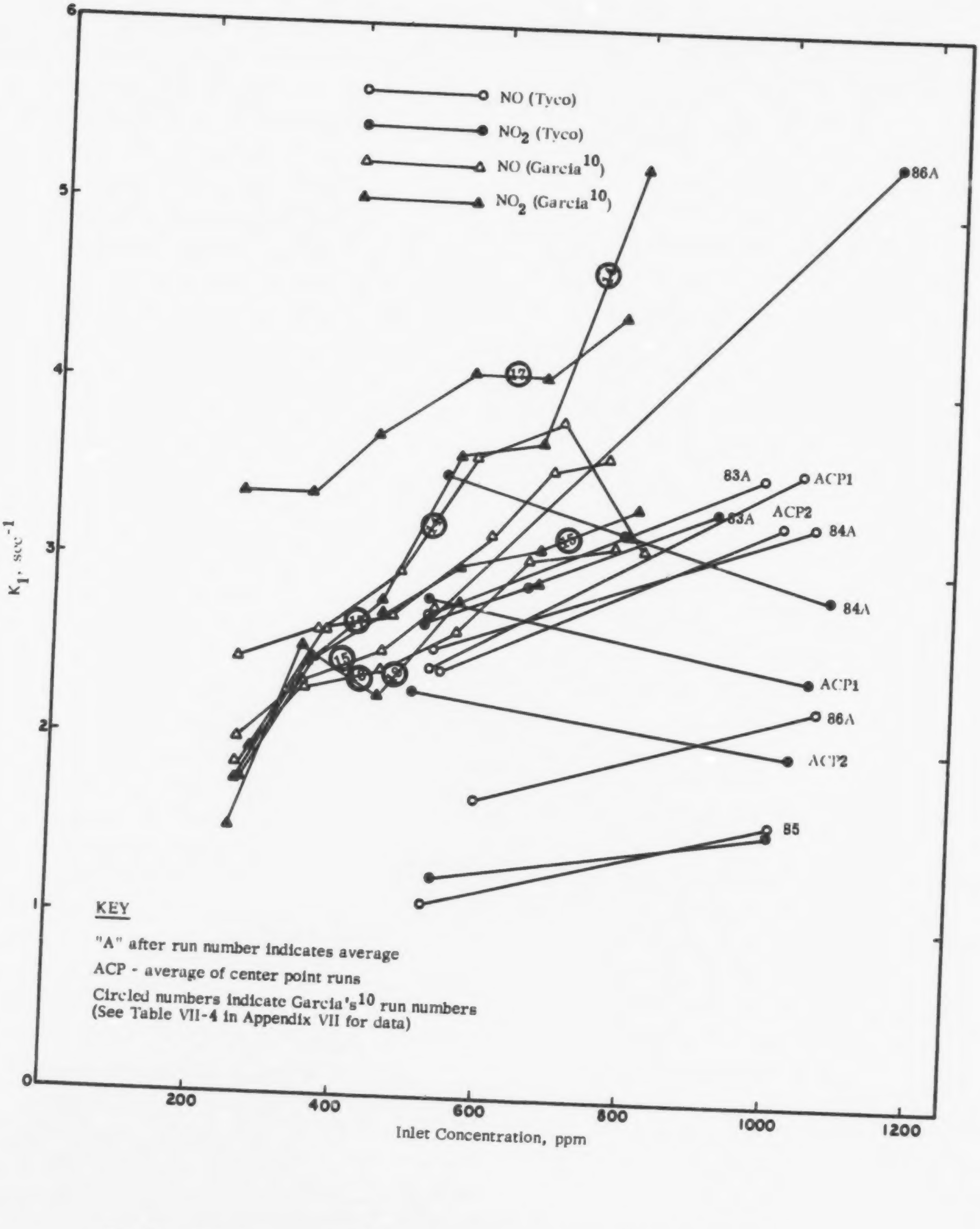

Fig. 28. First order reaction rate constant K_1 as a function of NO_x inlet concentration. Data from Tyco and EPA (Garcia^{10}).

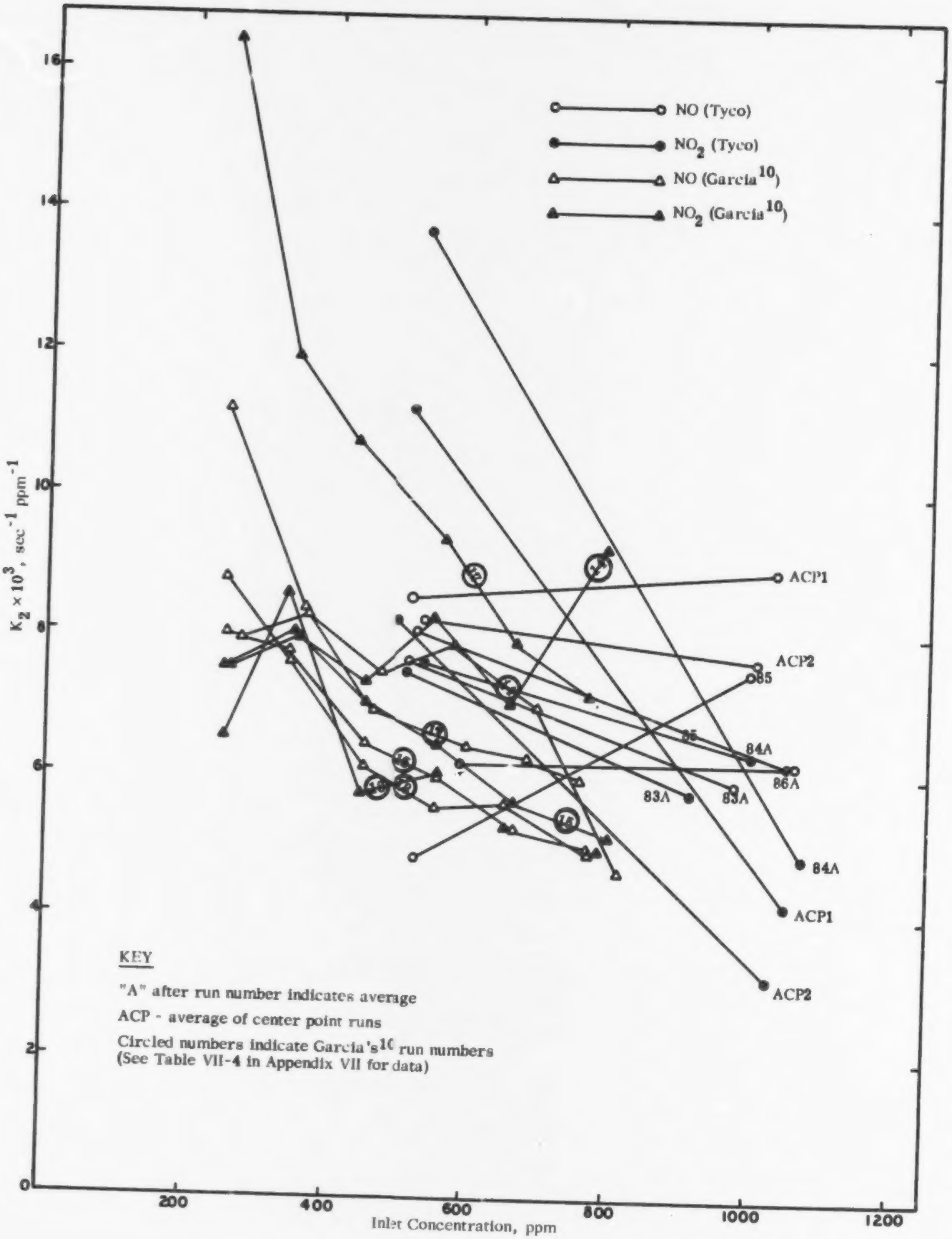

Fig. 29. Second order reaction rate constant K_2 as a function of NO_x inlet concentration. Data from Tyco and EPA (Garcia^{10}).

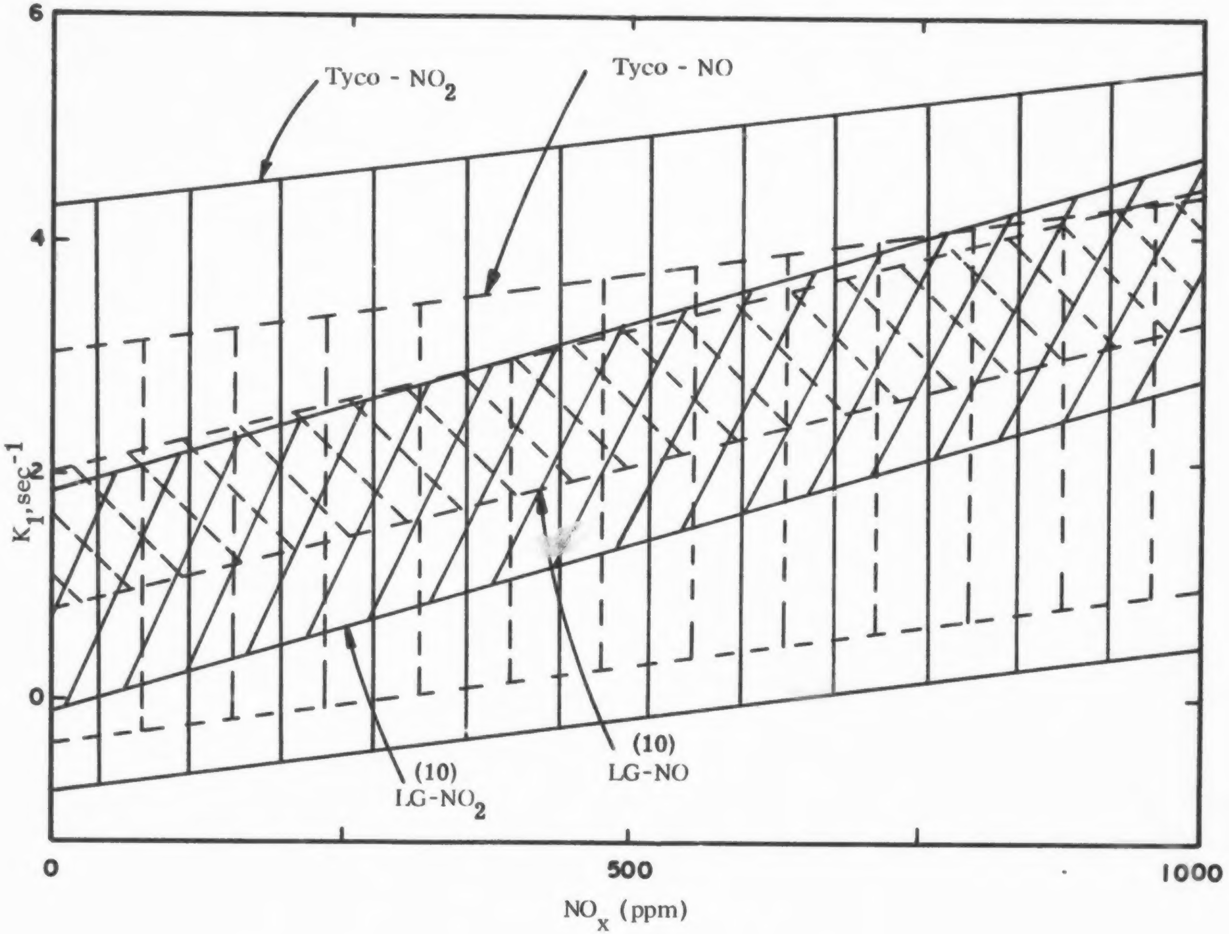

Fig. 30. Standard deviation for first order rate constant values, 95% confidence limits.

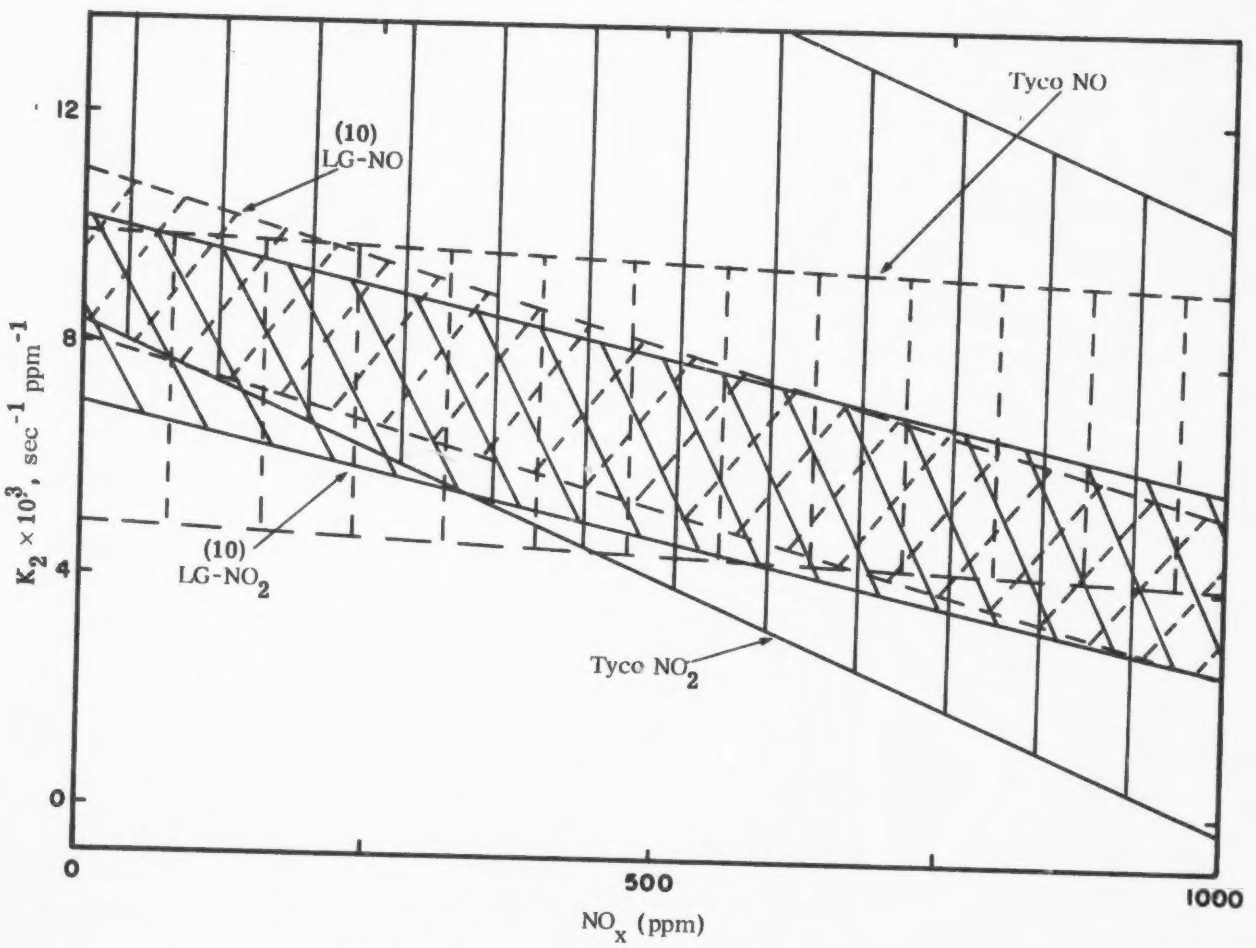

Fig. 31. Standard deviations for second order rate constant values.

nitrogen specie expected to be formed in the scrubber under neutral or alkaline conditions, such as prevailed in the OAP work. One would expect different rates of formation for these two species because of the wide variation in pH and water activity. If the formation of NO^+ or NO_2^- were rate limiting, we would have expected a difference in scrubbing rates. No difference was observed. Therefore, the theory that the gas phase reaction between NO and NO_2 is controlling is substantiated. Another factor is that considering the wide temperature range, one would have expected a wide fluctuation in scrubbing rate if the rate limiting step involved a liquid phase reaction.

The only rate limiting steps which we can imagine might be responsible for the observed results would be diffusion and gas phase formation of N_2O_3 followed by rapid dissolution. Bimolecular gas phase reactions can have low temperature coefficients (i.e., reaction rates may be a weak function of temperature), which would correspond with the observed results.

The Tyco and OAP scrubbing results may be applied to the design of a scrubber if one takes care not to extrapolate the derived rate constants too far from the concentration regions in which they were obtained. It is also necessary to use similar packing materials.

VII. STRIPPER EVALUATION

A. Initial Concept

The catalytic stripper stage of the Catalytic Chamber Process had the function of denitrating the acid effluent from the high temperature scrubber and simultaneously oxidizing the nitrogen oxides to NO_2. Since the nitrogen oxides were absorbed as equimolar amount of NO and NO_2, this meant that half the NO_x had to be oxidized.

Experimentation during Contract CPA 70-59 indicated that exposure of the nitrose solution to the activated charcoal catalyst in a countercurrent stream of air resulted in a minimum of 99% denitration, with the off-gas being primarily NO_2. The process had not been evaluated quantitatively and the reaction mechanism had not yet been determined. The earlier experimentation had shown that the acid and air space velocities were critical parameters, and effective (although not optimum) values had been determined. Work during this contract was to more completely evaluate the stripper concept in both continuous miniplant tests and in batch laboratory scale experiments.

B. Laboratory Scale Stripper Tests

Several experiments were carried out with a stripper column made of 1-in. glass pipe with a total length of 3 ft. The packed portion of the column was 29 in. in length. A thermocouple well employing a thin-walled, 5-mm glass tube was situated at the center of the packed section. In the later experiments of this series, a thermocouple was also used to determine the feed nitrose temperature. Before this, feed nitrose was at ambient temperature. Nitrogen or air was used as the stripping gas and this was not preheated. Column packing was either 1/4-in. Intalox saddles or Witco no. 256 activated charcoal. Sulfuric acid concentration was nominally 80 wt %.

The goals of these batch tests were:

1. To compare the stripping action of inert and catalytic packings
2. To determine the maximum obtainable NO_2 level in the effluent gas
3. To obtain an insight into the stripper mechanism

The results of these initial experiments are given in Appendix VIII, Table VIII-1.

Intalox saddles were used as the column packing for Runs 1 through 17. The sample lines were not properly heated for these runs so that in cases where the NO_2 level is unexpectedly low, one must allow for the probability of nitric acid formation in the sample lines, thereby creating NO_2 analysis errors. This would be expected at temperatures where the partial pressure of water was higher than about 20 torr or, in our case, for column temperatures in the range of 280 to 300 °F. The most significant observation that can be made regarding saddles is that less than 10% stripping of the nitrose occurs at temperatures of 70 to 185 °F with either nitrogen or air. At 280 to 300 °F, about 50% denitration is accomplished with nitrogen and about 90% with air.

In contrast, significant stripping of nitrose solutions is achieved on activated charcoal, even at room temperature, with either nitrogen or air. At 185 °F, the stripping was generally above 90%. With nitrogen as a stripping gas, large quantities of NO and small quantities of NO_2 were observed. With air, the reverse was true.

The maximum steady state levels of NO_2 which were obtained were approximately 3%. However, higher levels were obtained when: (1) the acid sample was taken (pressure decrease in column), (2) the column was flooded (Run 33), or (3) the column temperature was increased. In these cases, momentary high levels of up to 10% were observed. Observations of the sort mentioned above tend to indicate that the NO_2 absorbs onto the activated charcoal, but that it can be displaced by oxygen if the nitrose flux is not too great and if the air flux is high enough. Unless the NO_2 is displaced, there seems to be a tendency for the NO_2 to be reduced to NO. Thus, enrichment of the stripper gas with oxygen might very well enable us to obtain higher steady state levels of NO_2.

To follow up the experimentation in the 1-in. column, a series of experiments were run in the 2-in. laboratory stripper in order to evaluate the capability of the stripper to produce a gas stream containing higher concentrations of NO_2. The data obtained during this limited experimentation are shown in Table VIII-2 in Appendix VIII.

The data reveal two significant points: almost complete denitration is easily achieved, and the effluent gas stream containing about 3% NO_2 with fairly poor material balance closure. In view of later developments in the interpretation of the output of the duPont UV photometer (see Appendix IX), it is quite likely that the NO_2 concentration is considerably higher than the figures shown in Table VIII-2. This is due to the fact that the 15-in. cell which was used during these tests cannot give accurate analyses above about 2% NO_2. The calibration curve tends to increase to a peak and then decrease, making it difficult to determine which side of the peak should be used to interpret the absorption reading. Use of the 1.5-in. cell eliminates this problem, and tests run in the miniplant strippers usually give better material balances. It is significant to note that the percentage of NO in the stripper gas effluent is quite low, usually less than 10% of the NO_2.

C. Miniplant Experimentation

Data concerning stripper performance is shown in the combined scrubber/stripper data sheets in Appendix IV. Two primary conclusions can be drawn from the data: high denitration yields are generally achieved, but the gaseous effluent contains a very high proportion of NO and very little NO_2. Although several experiments were run in the miniplant to try to reverse this proportion, there was usually an excess of NO present. The results showing high NO concentrations were contrary to laboratory scale test data and necessitated an in-depth examination of the stripper mechanism.

D. Analysis of Stripper Mechanism

Since more than half of the effluent NO_x was in the form of NO, there must be some reductive reaction occurring in the stripper. One possible reaction would be the reduction of NO_2 or $HNSO_5$ to NO by reaction with the activated carbon, e.g.:

$$4HNSO_5 + C + 2H_2O \rightarrow CO_2 + 4NO + 4H_2SO_4 .$$

If this were the case the off-gas would show CO_2. The long path (one meter) infrared batch cell was calibrated for CO_2 and the gas from several of the laboratory stripper runs (see Table VIII-1 in Appendix VIII) were analyzed for CO_2. The results of this analysis are shown in Table VII. One may calculate, using average values for Runs 38 through 41 (and using 2.83 ml/min of nitrose, of specific gravity, 1.73 g/ml containing 0.90 wt % $HNSO_5$), that if all of the $HNSO_5$ reacted with C to produce NO and CO_2, one would obtain a partial pressure of CO_2 corresponding to 1.943 cc/min of CO_2 or 0.0096 atm CO_2. This compares with the average measured value of 0.0095 atm CO_2.

This analysis leads to the conclusion that the activated charcoal is not acting as a catalyst, but is entering into a reaction with the nitrose to effect denitration. This is contrary to the experimental evidence developed earlier in the development of this process. Laboratory batch tests showed definite evidence of catalytic behavior of several materials in addition to carbon (see the Final Report for Contract No. CPA 70-59). Clearly, the results with carbon are not encouraging, but considerably more work would have to be done before the catalytic approach to denitration of nitrose is ruled out.

Table VII. CO_2 Analysis of Laboratory Stripper Tests*
(Feed gas CO_2 concentration =

Run	CO_2 (atm)
31	0.0344
34	0.0252
35	0.0143
38	0.0060
39	0.0144
40	0.0090
41	0.0085
42	0.0094
43	0.0058
44	0.0147
45	0.0118
46	0.0038

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* See Table VIII-1, Appendix VIII, for details of these experiments.

VIII. PROCESS CONTROL

A. Goals

One of the goals of this contract was to examine the Catalytic Chamber Process in terms of the process control that would be necessary to operate a full-scale plant. This task was taken on early in the development of the process because of two anticipated problems: the large scale of the gas handling system, and the need to accurately control the NO/NO_2 ratio to maintain an equimolar gas mixture in the feed to the high temperature scrubber.

The objectives of the process control studies were: (1) to determine the magnitude of upset conditions that the process must accommodate, (2) to determine how rapid detection and response must be to control the process during upset conditions, (3) to survey and assess the adequacy of existing and potential analytical and control equipment to satisfy the above requirements, and (4) to recommend a process control system to the EPA.

B. Power Plant Operating Conditions

To establish the magnitude of power plant upset conditions affecting the Tyco process, discussions have been held with TVA, Consolidated Edison Co. (N.Y.), and New England Power Co.

Discussions with William Thompson of TVA (Chattanooga) provided information on the operating conditions of a typical TVA coal-fired power plant. A summary of these discussions follows:

1. Turndown rate: Under normal controlled conditions, plant output is changed (turndown or turnup) at the rate of 3 MW/min for 125 to 550 MW power plants.

2. Normal operating schedule: Under normal operating conditions, a 550 MW power plant will deliver between 400 and 550 MW. Full load is usually delivered between 8 a.m. and 7 p.m., with the output being reduced after 7 p.m. Demand production and scheduling can be done on a weekly basis assuming normal operation.

3. Air control: Under normal operating conditions (between 400 and 500 MW), 130% excess air is used: 120% at the combustion zone and 10% at the stack. Air flow is controlled automatically to within 5%. When operating below normal conditions (200 to 400 MW), 140% excess air is used. There is considerable variation in air flow control under catastrophic turndown conditions.

4. Stack effluent properties: At full load, the flue gas analyzed about 7% water (assuming 10% water in the coal) and 2500 ppm SO_2 (3% S in the coal). NO_x is usually not determined. (The sulfur in the coal at the Shawnee plant varies between 1 and 4%. Thus, greater stack gas SO_2 fluctuations are noted on a week-to-week basis than on a day-to-day basis as sulfur varies with the coal shipment.)

5. Operating conditions: During normal operations, the load is changed by pulling one pulverizer out which would feed one level of burners in the furnace. The temperature of the burner is probably not changed, but the length of the burning zone varies, i.e., the height of the high temperature zone is reduced. When operating below normal power output (300 MW or lower), supplementary oil torches are needed. When coming up in temperature, the limiting factor is the metal temperature in the turbines. The output is therefore increased at a maximum of 3 MW/min even if the line voltage or grid voltage must change as a result. In the case of equipment failure, the following changes occur:

a. Turbine failure: 500 MW drops to 0 MW in seconds
b. Loss of one pulverizer: loss of 20-40 MW in seconds
c. Loss of pump: loss of 1/3 to 1/2 load in seconds

The plant can operate at 200 MW or less as repairs are made. Wide fluctuations of excess air would be experienced during equipment failure until control would be established manually to the desired level.

It must be noted that the power demand requirements on the TVA system do not normally fluctuate to the extent encountered by primarily urban electric utilities, such as the Consolidated Edison Co. of New York. To assess this factor, discussions were held with Joseph Cunningham, Plant Engineer, Astoria (N.Y.) Power Station, Consolidated Edison Co. Throughout these discussions, it was noted that despite the greater fluctuations in demand profile, the response rate of the equipment to such fluctuations, as well as operating conditions, are virtually identical.

Total generating capacity of Consolidated Edison (N.Y.) as of July 1, 1970, was 8,039 MW. The Astoria station, representing approximately 18% of Consolidated Edison's generating capacity, contains five units with nominal capacities as follows: unit 1 — 180 MW, unit 2 — 180 MW, unit 3 — 335 MW, unit 4 — 380 MW, and unit 5 — 380 MW. [Note: Units 1 — 3 were oil fired, unit 4 was being converted from coal to oil, and unit 5 was scheduled for conversion upon completion of unit 4.]

For the entire Consolidated Edison system, peak loadings occur during summer weekday afternoons between 3 and 4 p.m. Winter peaks occur from 5 to 6 p.m. as industrial and lighting loads overlap. Due to the mix of plant efficiencies present in older utilities, these system peaks are not necessarily reflected at the Astoria station. In practice, the least efficient generating units are turned on last and turned off first. Thus, the Astoria load profile, being buffered by the rest of the system, requires the nominal maximum output from 9 a.m. to 10 p.m.

Differences in generating efficiencies of units within a given station are also significant. The three larger generating units at Astoria operate at a higher efficiency than the two older units. Thus, the large units are operated at a continuous level throughout the day; changes in station output are made by thorough controlling of the smaller units. The interplay within units is shown most clearly in Fig. 32, which represents the operating parameters of one of the smaller (180 MW) units. Note the continuous daytime and evening operation at maximum levels. Dips in power output occur at noontime and after 10 p.m. Minimum levels are reached between 3 to 4 a.m.

1. Turnup and turndown rates: 2 to 4 MW/min is usually practiced, although the capability exists for controlled rates up to 8 MW/min. Control of process air feed is done automatically as with TVA.

2. Normal operation: The larger, more efficient units operate at their nominal maximum capacity 24 hr/day. The smaller, less efficient units follow the load profile described above. Minimum operating levels of 25% of unit capacity are used.

3. Air control: Units operating at the nominal maximum are run at 120 to 125% air. When run at reduced power, up to 150% air is used to maintain steam temperature. A 5 to 10% higher air excess is normally used in burning coal as compared to oil.

4. Equipment failure: The most common failure appears to be rupture of a boiler tube. Units are shut down during repairs. The effects of feed pump failures are dependent on the specific unit. The two smaller units have three pumps each. Pump failure thus results in the abrupt loss of about 40 MW. The three larger units operate with only one large pump each. Each unit has a 1/2-size backup pump which must be turned on immediately in the event the main pump fails. Rapid fluctuations in stack gas composition are to be expected in event of such failures as well as during startup operations. Startup times range from 3 to 6 hr (depending on unit size) before the unit can generate sufficient power to go on grid (minimum operating level). The unit continues up on grid at 2 to 4 MW/min (8 MW/min maximum) until it reaches the demand operating level.

A meeting was held with New England Power Co. concerning plant operating conditions as well as pilot plant site considerations. Section X discusses this meeting in detail; but, in general, the operating conditions and techniques did not vary significantly from those indicated above for TVA and Consolidated Edison.

C. Instrumentation Requirements

Regardless of the detailed control system selected, careful analysis of available analytical instrumentation will be required. Measurements of water, sulfur dioxide, nitrogen dioxide, nitric oxide concentrations, stream flow rates, and stream temperatures are currently expected to be mandatory in the final control scheme. A preliminary analysis of available instrumentation for the measurement of SO_2, NO_2, and NO has been carried out, with particular emphasis on automatic continuous analysis and control. Manufacturer's literature

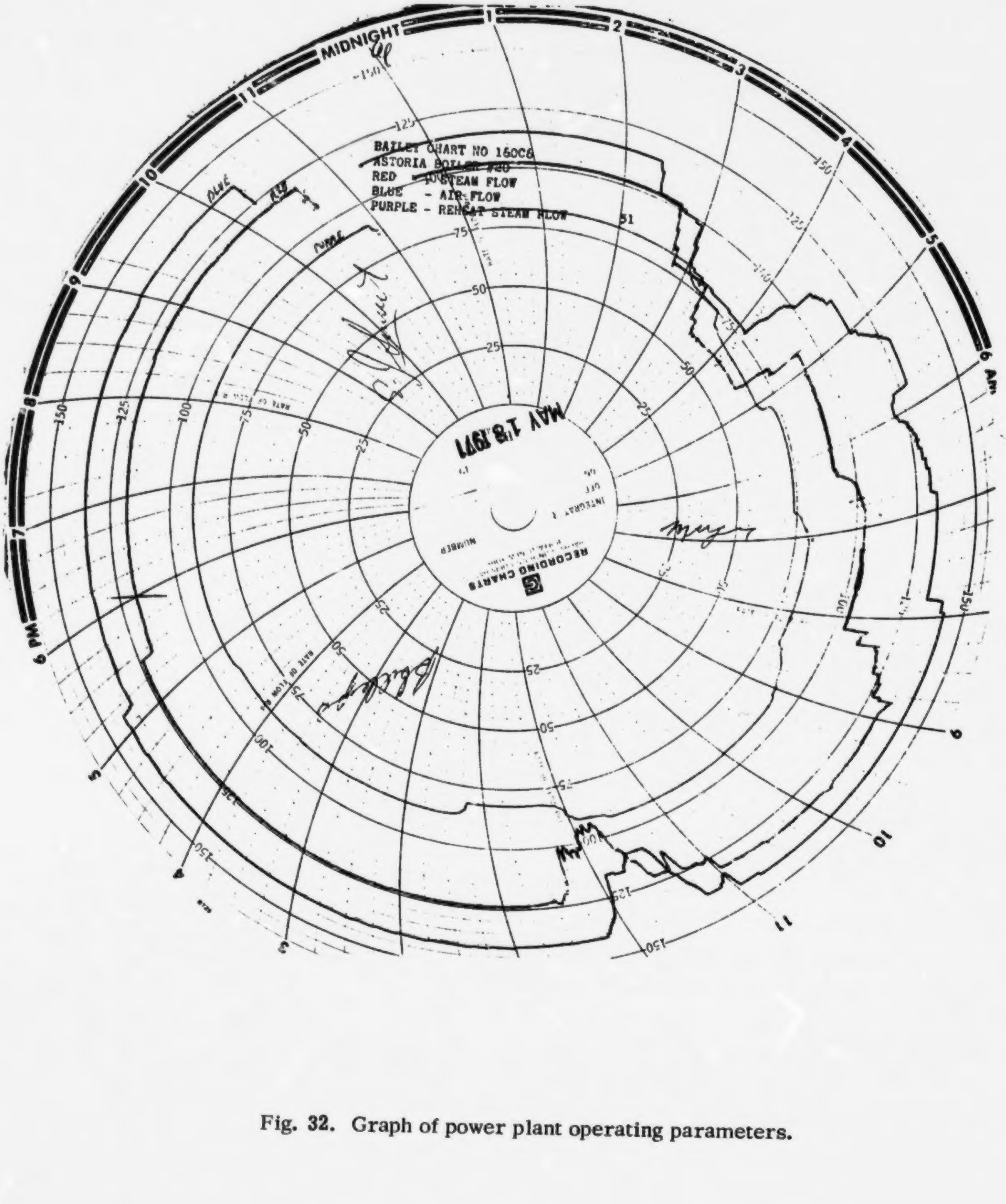

Fig. 32. Graph of power plant operating parameters.

was first surveyed to establish preliminary applicability. Where required, the appropriate technical assistance groups were contacted for more detailed information. Only instrumentation capable of being integrated with process control devices was considered in detail. The various analytical methods were organized into the following measuring techniques: spectroscopic, electrochemical, colorimetric (wet chemical), and gas chromatographic.

1. Spectroscopic instruments

Both Beckman and duPont produce spectroscopic instruments suitable for process control use. NO_2 and SO_2 are readily analyzed in the UV region using the 436 $m\mu$ and 302 $m\mu$ wavelengths, respectively. Although the instruments are basically similar in approach, the duPont 400 series photoanalyzer has the advantage that the sample cell can be run at elevated temperatures. The condensation of water and the resulting alteration of sample stream composition can thus be avoided.

Since NO is practically transparent in the UV region, IR analysis using the 5250 $m\mu$ band is usually used. Water interferes in the IR region; thus, the sample must first be passed through a cold trap or a desiccant for drying. The analysis is then carried out at ambient temperatures. Alternatively the NO may first be oxidized to NO_2 (using a charcoal catalyst and a source of oxygen) and the total NO_2 measured in the UV region. The measured NO levels, which are determined by differences in the NO_2 concentration before and after oxidation, would not be expected to be sufficiently accurate, particularly where low concentrations of NO must be determined.

The response rate of spectroscopic instruments to changes in concentration at constant sample stream flow is determined by the volume of the sample cell. The longer sample cells required for the measurement of lower concentration levels present the most serious limitation. However, worst case response times of 15 sec are quoted for instruments of this type. Instrument costs are on the order of $3,000 per installation.

2. Electrochemical methods

NO, SO_2, and NO_2, when dissolved in an electrolyte, are electrochemically active; i.e., they can be oxidized or reduced (in the case of NO_2 and SO_2) by the passage of an electrical current. Devices based on this principal are being sold by Dynasciences (a Division of Whittaker) and Environmetrics. Conversations with both manufacturers indicate that the devices are identical.

The sensor in all cases is a simple electrochemical cell consisting of a porous membrane, an electrolyte, and a reference electrode. The potential of the cell is maintained by an electronics package which also measures the current output (which is proportional to the quantity of sample reaching the cell). Sample temperatures are limited to 110 °F or less in order to avoid damage to the electrochemical device.

Both manufacturers claim devices which can measure the presence of SO_2 without interference from NO or NO_2. Units which measure NO_2 in the presence of SO_2 appear to require either a scrubber to remove the SO_2 or a separate SO_2 detector to null out the SO_2 current. Only Environmetrics claims to be able to measure NO independently of NO_2. The units are relatively inexpensive (\$250 for the sensor and \$2,000 for an electronics unit capable of handling two separate signals) and compact. Demonstrations of these devices are currently being arranged. Particular attention must be paid to problems (e.g., water condensation) inherent in the reduction of sample temperature. In this area, Dynasciences has a device available which uses a porous membrane to separate a portion of the gas to be measured from the hot stream. Cooling of this relatively dilute sample stream would not be expected to cause condensation.

Although rapid when compared to the process conditions, the response rate of this type of detector is significantly slower than that of the spectroscopic instruments. Depending on the details of sensor design which determine the diffusion rate of the dissolving gas, response times are reported to range up to several minutes for 90% of full-scale reading.

3. Colorimetric analysis

Many analytical devices based on the automation or semi-automation of the classical chemical techniques for the analysis of dissolved gases are available. Most of these units are designed for ambient (low ppm) levels of pollutant gases. Due to relatively long cycle times and/or limited concentration ranges, their application to source and process concentration levels is questionable.

4. Gas chromatography

This method may be divided into a measurement or detection stage and a column or separation stage. Automated gas sampling can be performed at the process stream temperature. Once a sample is taken, it can be readily transferred through heated tubing to the analytical column. Ideally, the column would first separate and isolate each gas component and pass them over a detector. The sensitivity of this detector determines the sensitivity of the method. The analytical column determines the selectivity. In principle, this method should have considerable versatility.

Commercial process control chromotographs (Bendix Corp., Applied Automation) typically include automated sample stream switching, multiple columns (to permit relatively complex separations), and thermal conductivity detectors, as well as the electronics required to convert what is basically a batch output (e.g., a peak area) into a trend-following signal which could be used for set-point control. Prices range from \$10,000 and up for installations capable of handling two or three sample points.

Instrument response times would be dependent on the cycle time of the particular analytical column being used. Thus, from both the process control and analytical standpoint, column selection presents the most difficult problem. Single column separation of NO_2, NO, and SO_2 in the presence of the other flue gas components is not likely. Although specific information was not obtained, Bendix Corp. claims to have experience in such separations using multiple column technology.

Based upon a survey of presently available instrumentation, it appears that instruments using spectroscopic measuring techniques are the only units sufficiently flexible in terms of operating range and temperature to allow their further consideration. The main advantages of the spectroscopic approach lies in the limited amount of sample preparation required as well as the inherently continuous output signal. The response of this instrument type is adequate for integration with process control devices.

D. Process Control Requirements

A preliminary evaluation of the major process control requirements (Fig. 33) was performed during the current contract. Three major control loops are shown: (1) reactor control, including control of NO/NO_2 ratio, (2) control of the L/G ratio in the scrubber, and (3) control of the NO_2 concentration in the stripper offgas. Also indicated is the overall control of process stream flows required to maintain the Tyco process in an operating mode subservient to that of the power plant.

Three conceptual design changes in the overall system were also made. First, note that the NO_2 recycle stream is introduced prior to the main process blower in order to take advantage of all available mixing capability. (Since the flow velocity in the process blower is quite high and since the stream temperatures are well above the dew point, corrosion problems in the blower should not be increased significantly.) A second alteration involves recycling of some of the acid wash (produced during fly ash concentration) into the scrubber. In addition to reducing subsequent neutralization costs, this procedure allows the scrubber to be operated at a higher temperature than that required to produce product acid at the desired concentration. Excess water is removed by the scrubber, but the concentration is closely controlled by adding the dilute acid wash back in. In this manner, small fluctuations in scrubber temperature will not seriously affect product acid concentration. The temperature control requirements involved in scrubber operation are therefore reduced. In addition, final modification places the power plant's stack fan after the isothermal scrubber.

1. Reactor control

As diagrammed, control of the oxidation reactor is obtained by adjusting the flow rate of the recycle NO_2 stream in order to maintain a constant 1:1 ratio of NO to NO_2 in the reactor output. Reactor response to changes in NO_2 and SO_2 inputs will be extremely fast (seconds), since the equivalent holdup time (determined by the rate constant of the reaction) is approximately 14 sec. An alternative to this feedback control approach, which avoids the measurement of NO (the more difficult analysis), is also possible. Feedforward control, based on measurements of SO_2 and NO_2 going into the reactor, is feasible if: (1) the ratio of NO_2 to NO in the power station flue gas is constant for all operating levels, (2) no reoxidation of NO occurs prior to the scrubber, and (3) a history of suitable emission control in the exit flue gas has been demonstrated.

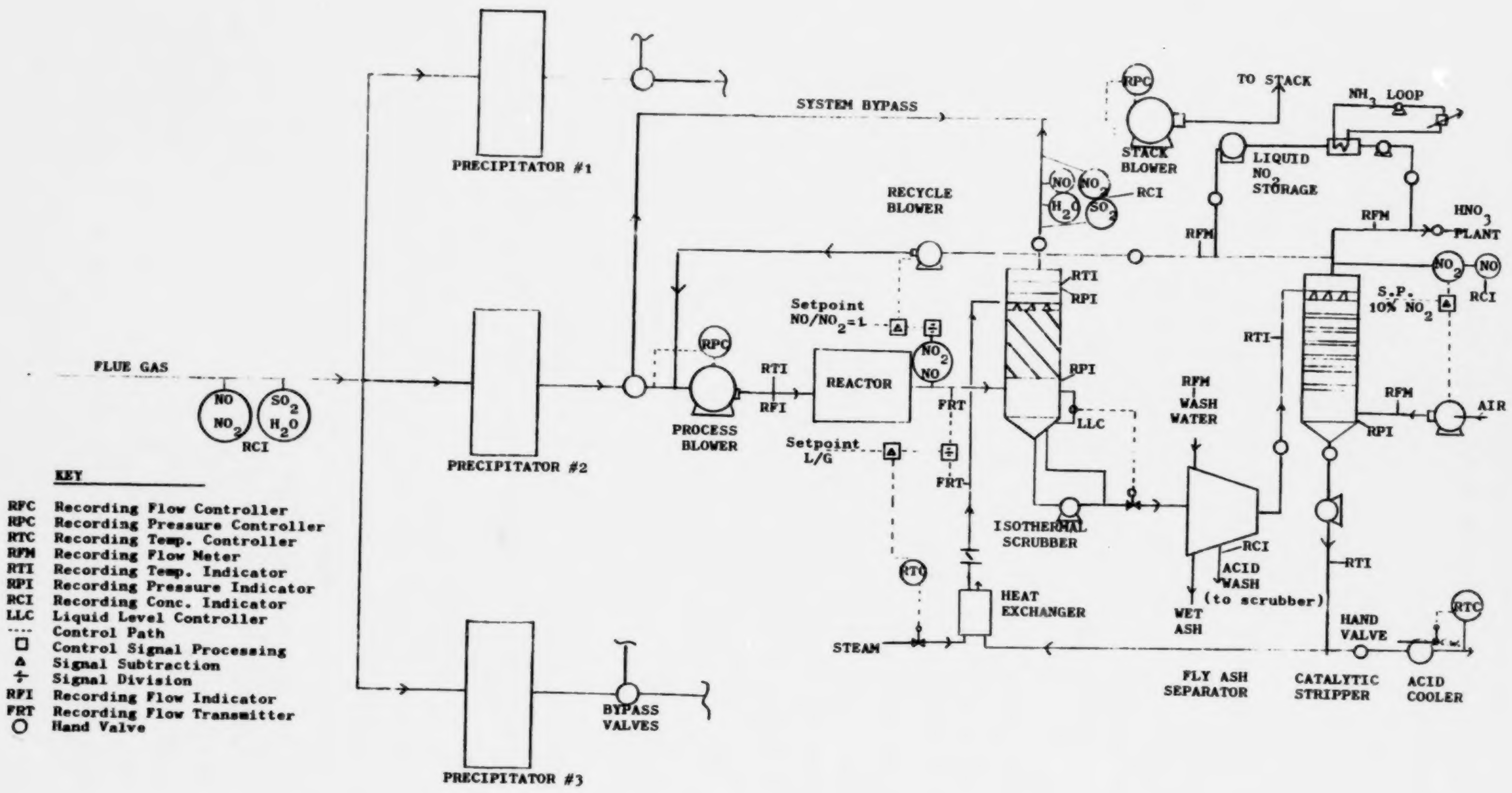
FLUE GAS
NO
NO2
SO2
H2O
RCI
PRECIPITATOR #1
PRECIPITATOR #2
PRECIPITATOR #3
BYPASS VALVES
SYSTEM BYPASS
PROCESS BLOWER
RPC
RTI
RFI
REACTOR
Setpoint NO/NO2=1
Setpoint L/G
NO2
NO
FRT
FRT
RTC
STEAM
HEAT EXCHANGER
RECYCLE BLOWER
RTI
RPI
RPI
LLC
ISOTHERMAL SCRUBBER
NO
NO2
H2O
SO2
RCI
RPC
STACK BLOWER
TO STACK
LIQUID NO2 STORAGE
NH3 LOOP
RFM
RFM
HNO3 PLANT
NO2
NO
RCI
S.P. 10% NO2
RFM
AIR
RPI
RTI
RFM
WASH WATER
RCI
ACID WASH (to scrubber)
WET ASH
FLY ASH SEPARATOR
RTI
HAND VALVE
RTC
CATALYTIC STRIPPER
ACID COOLER
KEY
RFC Recording Flow Controller
RPC Recording Pressure Controller
RTC Recording Temp. Controller
RFM Recording Flow Meter
RTI Recording Temp. Indicator
RPI Recording Pressure Indicator
RCI Recording Conc. Indicator
LLC Liquid Level Controller
---- Control Path
□ Control Signal Processing
▲ Signal Subtraction
÷ Signal Division
RFI Recording Flow Indicator
FRT Recording Flow Transmitter
○ Hand Valve

Fig. 33. Major process control requirements.

2. Scrubber control

By designing the scrubber to handle the maximum possible flue gas flow at the desired operating efficiency, scrubber control is reduced to a simple maintenance of the L/G ratio. As long as the L/G ratio is held constant (by controlling the acid feed from the stripper), it is anticipated that scrubber efficiency will be maintained at all operating levels.

3. Stripper control

Here again, the control system is simplified by ensuring adequate stripper capacity to handle the maximum nitrose flow. A feedback loop adjusts a variable speed blower to obtain 10% NO_2 in the stripper offgas. As designed, that portion of the 10% NO_2 stream not required by the SO_2 oxidation reactor is diverted to the nitric acid plant. The flow rate to the acid plant is thus subject to variations dependent on the flue gas input. It is possible to maintain a constant flow rate in this stream (by bleeding additional air into the stripper off gas), but constancy of both flow and composition is impossible. The preferred operating mode of the nitric acid plant will determine whether the constant flow rate or composition control is preferable.

An evaluation was also made on suitable startup procedures. In general, power station outages from key facilities are infrequent, let us say 1 to 2 times per year. However, once they occur (through either equipment failure or scheduled maintenance), downtimes on the order of days to weeks may be expected. During these intervals, the Tyco process must be maintained in a mode capable of relatively rapid startup.

The overriding criteria during both startup and standby operation are the maintenance of operating temperatures (to ensure rapid and efficient startup) and the storage of NO_x (to avoid both further expense and contamination).

Storage of the NO_x can be accomplished most easily in a low pressure liquid NO_2 tank. During normal process operation, the tank is filled by routing stripper offgas through a compressor and ammonia chilled condenser. Since NO_2 is a liquid at 70 °F and 1 atm pressure, elaborate pressure vessels are not required. As is indicated in Fig. 35, the operating temperature of the scrubber and stripper will be maintained by circulating sulfuric acid (any nitrose will be removed by the stripper) through a steam heat exchanger.

In the event of a power station outage, the flue gases are first bypassed directly to the stack blower. The acid loop heat exchanger is then activated to maintain operating temperature. $HNSO_5$ present in the acid loop is removed by the hot stripper and sent to either NO_2 storage or to the HNO_3 plant. Once the $HNSO_5$ is removed, the stripper blower will turn off. Pure H_2SO_4 will continue to circulate until the system is reactivated.

System startup is accomplished by allowing the hot flue gas to pass through the reactor and scrubber. NO_2 is bled directly from the NO_2 tank so as to maintain the proper NO/NO_2 ratio at the reactor outlet. Effective scrubbing and stripping can commence immediately since the units are maintained at their operating temperature. The NO_2 (from storage) can be shut off once the stripper offgas reaches the 10% NO_2 level. The length of this period will be determined by the $HNSO_5$ holdup in the acid system.

Once the system has stabilized, the NO_2 level in the storage tank can be replenished by diverting the stripper offgas through the condenser. Thus, both startup length and frequency will determine the NO_2 storage requirements. Obviously, initial startup of the Tyco process can be effected through the use of purchased NO_2.

Tank storage of the NO_x values as a nitrose solution has also been considered. System startup would be accomplished by bleeding the stored nitrose solution directly into the stripper. If the stripper is bypassed during standby operation, the nitrose can be stored in the acid loop itself. In this case, the scrubber would have to be started with a hot stream of pure H_2SO_4 (from storage) in order to avoid stripping of the nitrose solution during process startup. A major advantage of nitrose storage is that it permits the scrubber to be constructed from less expensive materials which are passive in nitrose solutions. Use of such materials would, of course, reduce plant investment.

Selection between the alternative methods of NO_x storage must consider the economics of each approach. Without further experimental backup at the 2000 SCFM level, it is premature to select the ultimate NO_x storage technique.

IX. ECONOMIC EVALUATION

A. Prior Evaluations

Economic evaluations of the Tyco Catalytic Chamber Process have been made earlier in the development of the process by Tyco and by the Tennessee Valley Authority (TVA) (under contract to OAP). Both analyses showed a required investment of about $12 to $16 million for removal of 90% of the SO_2 and 60% of the NO_x from an 800 MW coal burning power station whose stack gas contained about 2200 ppm of SO_2 and 600 ppm of NO_x. Based on the salability of sulfuric and nitric acid, at $12 and $40 per ton (100%), respectively, the add-on facility would operate at about the break-even level. (See the final report for Contract No. CPA 70-59 for details of this economic analysis.)

During the contract discussed in this report, an initial economic analysis of the process used only for NO_x removal was presented to OAP. (A suggested flowsheet is presented in Fig. 34.) Assuming 75% removal of 600 ppm NO_x and the manufacture and sale of nitric acid, the plant would cost about $12 million and would add $1.48 per ton of coal to the operating cost of a 500-MW power station. Details of this analysis are shown in Tables VIII, IX, and X. The analysis was based on the experimental data from Contract CPA 70-59.

B. New Process Concept

As a result of the experimentation performed on this contract, there has been a change in the process concept as well as an overall enlargement of the plant size. The conceptual change involves the use of a liquid phase reactor to oxidize the SO_2. This reactor would be larger than the one used in previous process evaluations and would be more costly because of the need for either packing or spray tower construction. Fig. 35 shows a proposed flowsheet utilizing the new reactor concept.

1. Reactor cost

It is difficult to size the new reactor because of the limited amount of data available, but assuming the 14-sec residence time required in the miniplant for 90% reaction yields, we would need about 1000 ft of columns. These could be set up as 20 columns, 25 ft in diameter and 50 ft high, packed with 3-in. Intalox saddles. The estimated cost of such columns would be about $6 million. Further optimization of reactor design and contact methods should reduce the residence time and reactor cost.

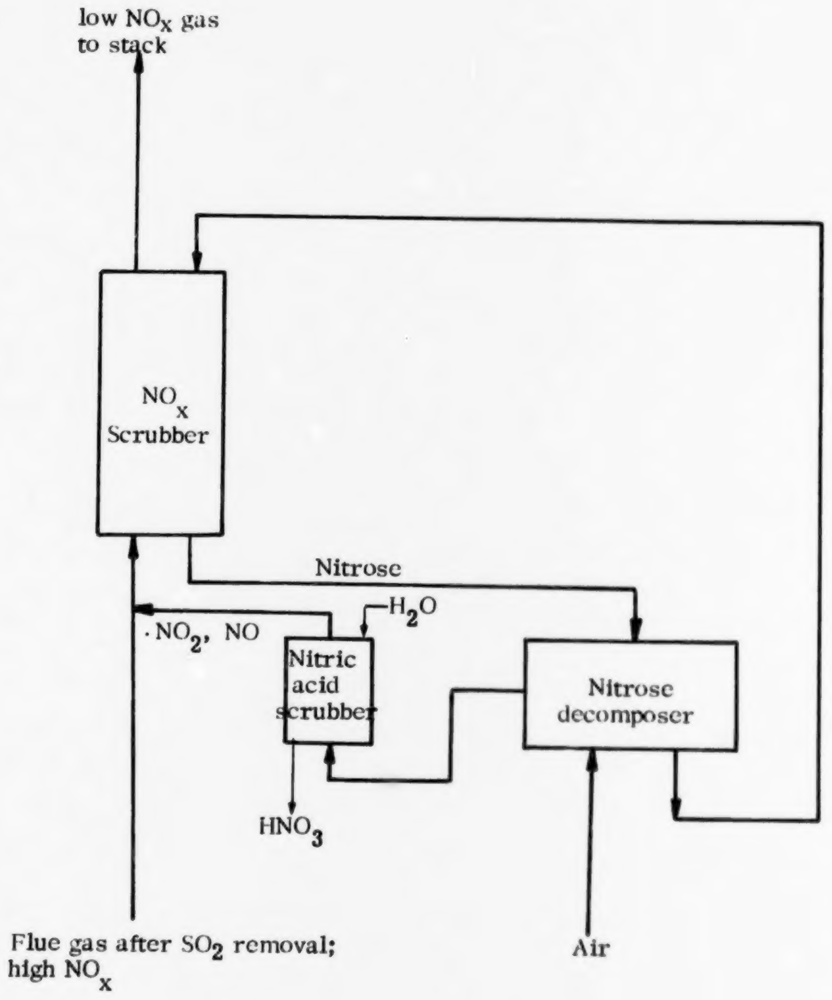
low NO_x gas to stack
NO_x Scrubber
Nitrose
H_2O
NO_2, NO
Nitric acid scrubber
Nitrose decomposer
HNO_3
Flue gas after SO_2 removal; high NO_x
Air

Fig. 34. Flowsheet showing the Tyco Catalytic Chamber Process used for NO_x removal only.

Table VIII. Economics of NO_x Scrubbing Plant for 500-MW Power Plant* Based on Tyco SO_2 Removal Process

Estimated Major Equipment Cost

Item	Use	No.	Size	Cost
1. Scrubber	NO_x scrubbing	4	250,000 SCFM 20 ft dia 40 ft high	$1,500,000
2. Packing	For Item 1 - Scrubber	12,000 ft^3 ea.	3" Intalox Saddles	500,000
3. Stripper	Denitrification	2	20 ft dia 30 ft high	500,000
4. HNO_3 Absorber	HNO_3 Production	1	30 ft dia 60 ft high	400,000
5. Filter	Remove ash from acid	4		250,000
6. Product Storage Tank	Hold HNO_3	2	50,000 gal 15 × 40 or 20 × 22	50,000
7. Exhaust Fan	Provide differential pressure	4	~12" H_2O	100,000
8. Pumps	2 stages of pumping to scrubber and to stripper	–	Total 54,000 GPM	150,000
			TOTAL	$3,450,000

Use Lange Factor of 3.5

Total Installed Cost = $3.5 \times 3.45 \times 10^6$ = **$12,100,000**

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*1×10^6 SCFM
600 ppm NO_x (75% recovery)

Table IX. Economics of NO_x Scrubbing Plant for 500-MW Power Plant Based on Tyco SO_2 Removal Process

Annual Operating Costs

Materials		
Charcoal replacement		$ 500,000
Direct Labor		110,000
Supervision		30,000
Maintenance	5% of fixed capital	605,000
Supplies	15% of maintenance	90,800
Utilities		
Power		250,000
Water		10,000
Heat	(startup only)	50,000
TOTAL DIRECT COST		$1,645,800
Payroll Burden	(20% of direct labor and supervision)	28,000
Plant Overhead	(50% of direct labor, supervision, maintenance, and supplies)	417,900
Packing and Shipping		100,000
Waste Disposal		50,000
TOTAL INDIRECT COST.		$ 567,900
Depreciation	(10% of fixed capital) non-regulated (regulated: $403,000)	1,210,000
Taxes	(2% of fixed capital)	242,000
Insurance	(1% of fixed capital)	121,000
TOTAL FIXED COST.	non-regulated. . . . . (regulated: $766,000)	$1,573,000
TOTAL OPERATING COST.	non-regulated. . . . . (regulated: $2,979,700)	$3,786,700

Table X. Economics of NO_x Scrubbing Plant for 500-MW Power Plant Based on Tyco SO_2 Removal Process

Net Process Cost

Credit	19,100 tons/yr (100% HNO_3) at $40/ton		$764,000
Net Cost	(regulated)	$2,979,700 - 764,000 $2,215,700	
	or $\frac{\$2{,}215{,}700/\text{yr}}{1{,}500{,}000 \text{ tons coal/yr}}$		$1.48/ton coal
Net Cost	(non-regulated)	$3,786,700 - 764,000 $3,022,700	
	or $\frac{\$3{,}022{,}700/\text{yr}}{1{,}500{,}000 \text{ tons coal/yr}}$		$2.02/ton coal

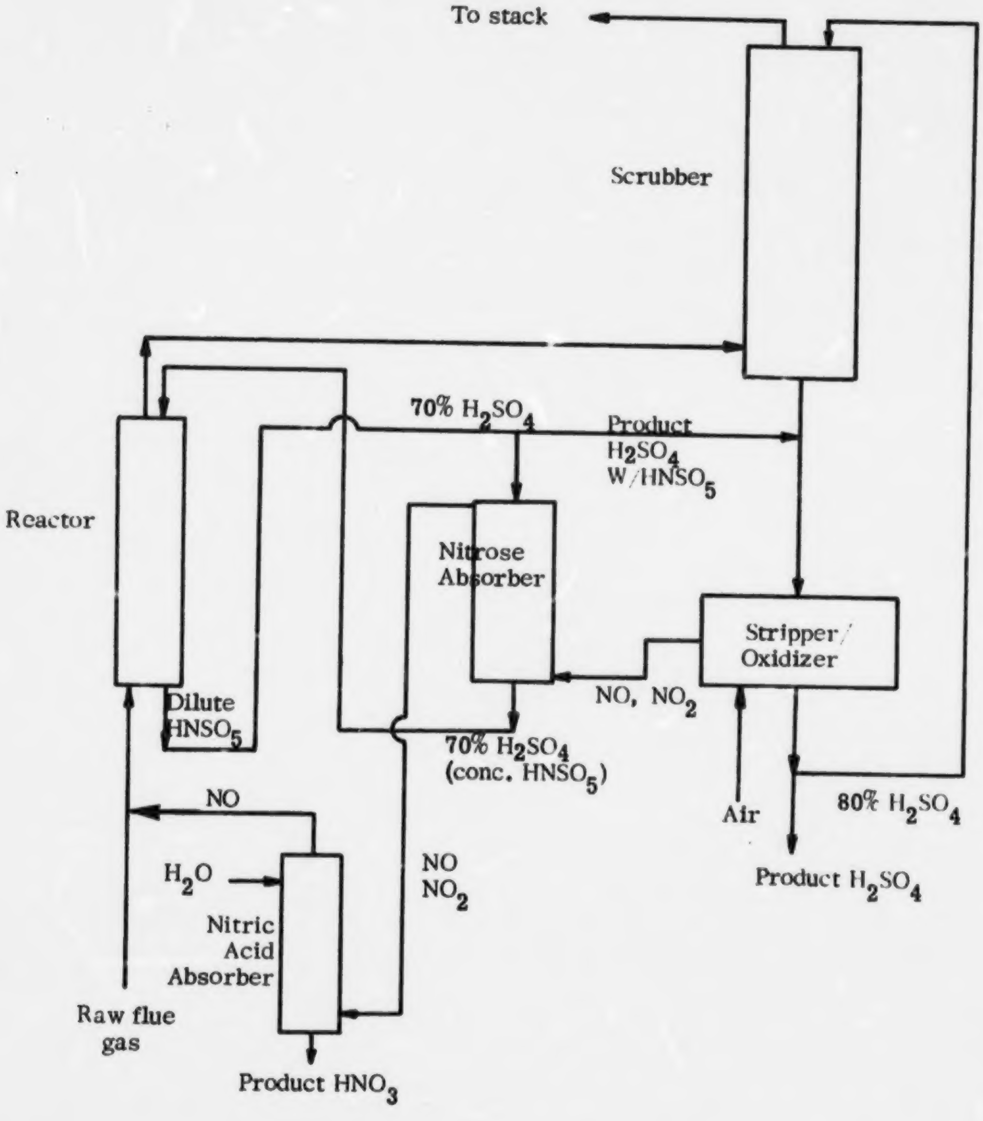
To stack
Scrubber
70% H_2SO_4
Product H_2SO_4 W/$HNSO_5$
Reactor
Nitrose Absorber
Stripper/ Oxidizer
NO, NO_2
Dilute $HNSO_5$
70% H_2SO_4 (conc. $HNSO_5$)
NO
Air
80% H_2SO_4
H_2O
NO NO_2
Product H_2SO_4
Nitric Acid Absorber
Raw flue gas
Product HNO_3

Fig. 35. Proposed flowsheet for Catalytic Chamber Process utilizing a wetted reactor for SO_2 oxidation.

2. Scrubbing Costs — SO_2/NO_x Removal

If the process were used for removing both SO_2 and NO_x, it would be necessary to have packed towers about 105 ft high to reduce the concentration of NO_x from 6000 ppm total NO plus NO_2 to 100 ppm total NO_x. This figure is developed from visual extrapolation of data produced in Run 92 (see Appendix IV), as shown in Fig. 36. If we assume an L/G of 5.0 moles/mole and a gas flow of 282 $lb/hr\text{-}ft^2$ as used in the miniplant experimentation, we would need about 53 columns 25 ft in diameter and 105 ft high, packed with 3-in. Intalox saddles (although it would be better to use 106 columns half as high to avoid ground loading problems). These shorter columns would cost about $1 million each for a total purchased cost of $106 million. Assuming a 3.5 factor for installation and auxiliary equipment, the scrubbing facility alone would cost about $370 million, clearly an unreasonable expense for this process. The total capital and operating expenditures are estimated in Tables XI and XII.

Typical commercial operation of a packed column, such as the scrubber, is at 75% of flooding. If it can be assumed that subsequent process optimization would allow operation at 75% of flooding with the same L/G and column height, we would then need 12 columns 25 ft in diameter and 105 ft high, packed with 3-in. Intalox saddles, or 24 columns half as high. The purchased cost of these columns would be about $24 million or about $84 million installed. The entire plant would cost about $114 million, as shown in Table XIII, or over $140/KW installed for an 800-MW power plant. Estimated operating costs are shown in Table XIV. Comparison of Tables XI and XII with XIII and XIV show how strongly dependent the capital and operating costs are on scrubbing efficiency. Economical implementation of the Catalytic Chamber Process clearly depends on increasing the scrubber gas loading and decreasing the reactor residence time.

C. Cost of NO_x Removal Only

In sizing the scrubbing facility for removing NO_x only, the same two scrubber flow rates were used as with the combined SO_2/NO_x system discussed above. The data from Runs 85c, 96c, 92c, and 96c indicate that about 90% of an equimolar NO/NO_2 gas stream containing 1000 ppm of each can be removed in about 27 ft of packing at an L/G of about 5.0 moles/mole and a gas mass flow rate of 282 $lb/hr\text{-}ft^2$. Extrapolation of the data, as shown in Fig. 37, indicates that the gas could be cleaned to 100 ppm total NO_x in about 45 ft of packing. The cost of a plant to accomplish this would be about $175 million, with an annual operating cost of about $41.0 million (8.5 mils/KWhr). See Tables XV and XVI for details.

If we again assume that optimization of the system would allow us to operate at 75% of flooding with a similar column height in the scrubber, we would need less scrubbing capacity and the plant cost would drop to $43.5 million. The operating cost would then be $10.82 million or 2.3 mils/KWhr. Tables XVII and XVIII present the breakdown of this analysis.

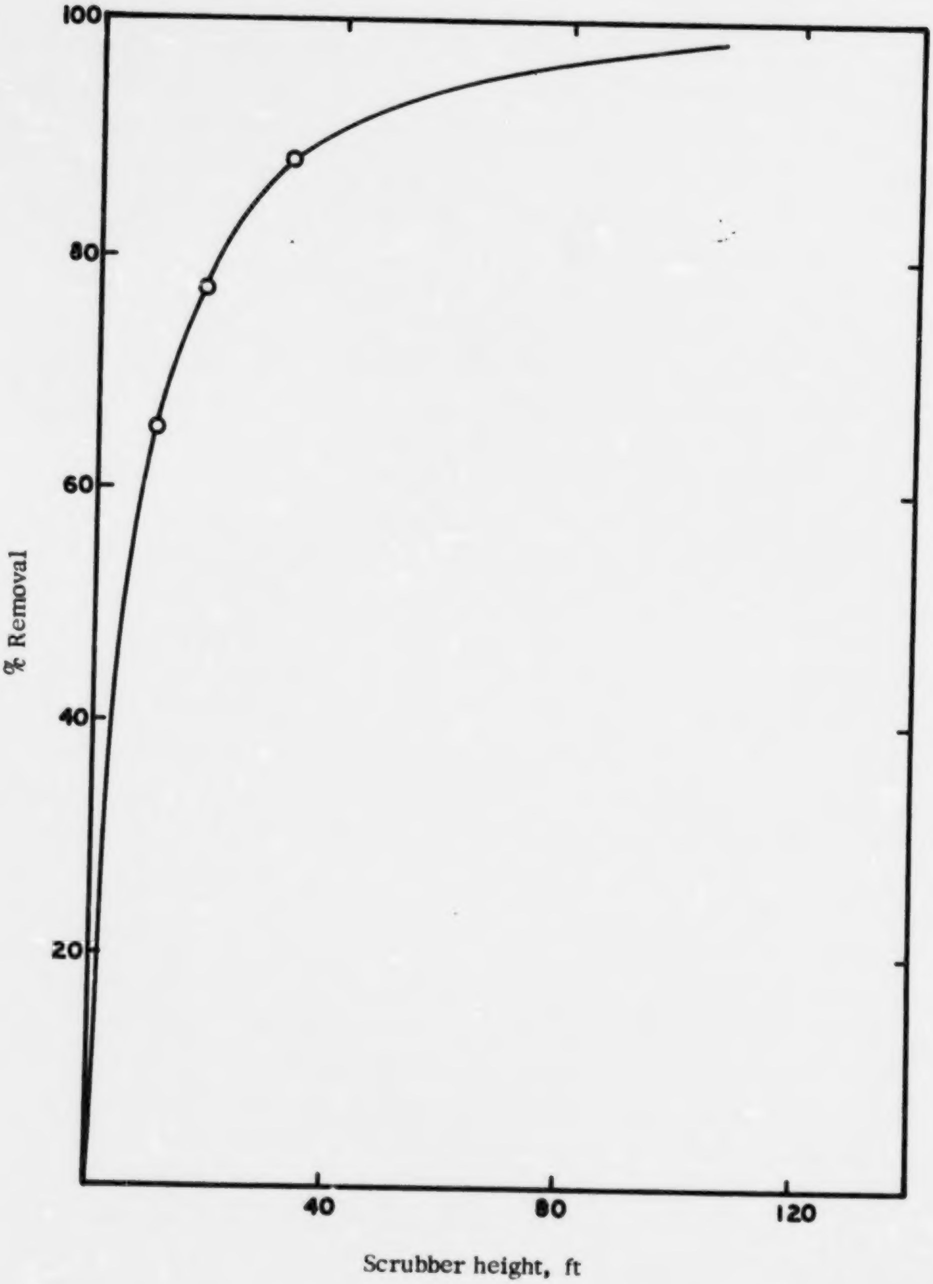

Fig. 36. Extrapolation of data from Run 92 to give scrubber column height for reducing NO_x concentration from 6000 ppm to 100 ppm.

Table XI. Economics of SO_2/NO_2 Scrubbing Plant for 800-MW Power Plant

Tyco Catalytic Chamber Process

Estimated Major Equipment Cost

Basis: 282 lb gas/ft^2-hr (Miniplant data)

	Item	Use	No.	Size	Cost
1.	Scrubber	NO_x scrubber	106	27,000 SCFM 25 ft dia 53 ft high packed with 3-in. Intalox saddles	$ 106,000,000
2.	Stripper	Acid denitrification	16	20 ft dia 30 ft high	4,000,000
3.	HNO_3 Absorber	HNO_3 production	1	30 ft dia 60 ft high	400,000
4.	Filter	Remove ash from acid	8	--	350,000
5.	Product Storage Tanks	Hold HNO_3 and H_2SO_4	8	50,000 gal	200,000
6.	Exhaust Fan	Provide differential pressure	8	12-in. H_2O	300,000
7.	Pumps	3 stages of pumping to scrubber, stripper, and reactor		Total 85,000 GPM	400,000
8.	Reactor	Oxidize SO_2	20	50 ft high 25 ft dia	6,000,000
9.	Nitrose Absorber	Nitrose production for reactor feed	1	15 ft dia 40 ft high	250,000
					$ 118,900,000

Using Lange Factor of 3.5:
TOTAL INSTALLED COST = $ 413,000,000

Table XII. Economics of SO_2/NO_x Scrubbing Plant for 800 MW Power Plant*

Tyco Catalytic Chamber Process

Annual Operating Costs

Basis: 282 $lb/hr\text{-}ft^2$ scrubber gas flow (Miniplant data)

Catalyst replacement (2 replacements per year)		$ 2,000,000
Direct labor		250,000
Supervision		75,000
Maintenance	5% of fixed capital	20,600,000
Supplies	15% of maintenance	3,100,000
Utilities		
Power		4,000,000
Water		100,000
Heat (startup only)		100,000
TOTAL DIRECT COST		$ 30,325,000
Payroll burden (20% of direct labor and supervision)		65,000
Plant overhead (50% of direct labor, supervision, maintenance, and supplies)		**12,013,000**
Packing and shipping		100,000
Waste disposal		50,000
TOTAL INDIRECT COST		**$ 12,228,000**
Depreciation (10% of fixed capital; non-regulated)		41,300,000
Taxes	(2% of fixed capital)	8,260,000
Insurance	(1% of fixed capital)	4,130,000
		$ 53,690,000
TOTAL OPERATING COST (non-regulated)		**$ 96,243,000**

or **19.8** mil/KWhr

* 330 days of operation per year at 75% capacity

Table XIII. Economics of SO_2/NO_x Scrubbing Plant for 800-MW Power Plant

Tyco Catalytic Chamber Process

Estimated Major Equipment Cost

Basis: 75% of flooding in scrubber

Item	Use	No.	Size	Cost
1. Scrubber	NO_x scrubbing	24	120,000 25 ft dia 53 ft high packed with 3-in. Intalox saddles	$ 24,000,000
2. Stripper	Acid denitrication	4	20 ft dia 30 ft high	1,000,000
3. HNO_3 Absorber	HNO_3 production	1	30 ft dia 60 ft high	400,000
4. Filter	Remove ash from acid	8	--	350,000
5. Product Storage Tanks	Hold HNO_3 and H_2SO_4	8	50,000 gal	200,000
6. Exhaust Fan	Provide differential pressure	4	~ 12-in. H_2O	150,000
7. Pumps	3 stages of pumping to scrubber, stripper, and reactor	-	Total 85,000 GPM	250,000
8. Reactor		20	50 ft high 25 ft dia	6,000,000
9. Nitrose Absorber	Nitrose production for reactor feed	1	40 ft high 15 ft dia	250,000
				$ 32,700,000
Using Lange Factor of 3.5: TOTAL INSTALLED COST =				$ 114,000,000

Table XIV. Economics of SO_2/NO_x Scrubbing Plant for 800 MW-Power Plant*

Tyco Catalytic Chamber Process

Annual Operating Costs

Basis: 75% of flooding in scrubber

Catalyst replacement (2 replacements per year)		$ 500,000
Direct labor		150,000
Supervision		50,000
Maintenance	5% of fixed capital	5,700,000
Supplies	15% of maintenance	850,000
Utilities		
Power		1,000.000
Water		25,000
Heat (startup only)		50,000
TOTAL DIRECT COST		8,275,000
Payroll burden (20% of direct labor and supervision)		40,000
Plant overhead (50% of direct labor, supervision, maintenance, and supplies)		3,375,000
Packing and shipping		100,000
Waste disposal		50,000
TOTAL INDIRECT COST		3,565,000
Depreciation (10% of fixed capital; non-regulated)		11,500,000
Taxes	(2% of fixed capital)	2,300,000
Insurance	(1% of fixed capital)	1,150,000
		$ 14,950,000
TOTAL OPERATING COST (non-regulated)		$ 26,790,000
	or 5.5 mil/KWhr	

* 330 days of operation per year at 75% capacity

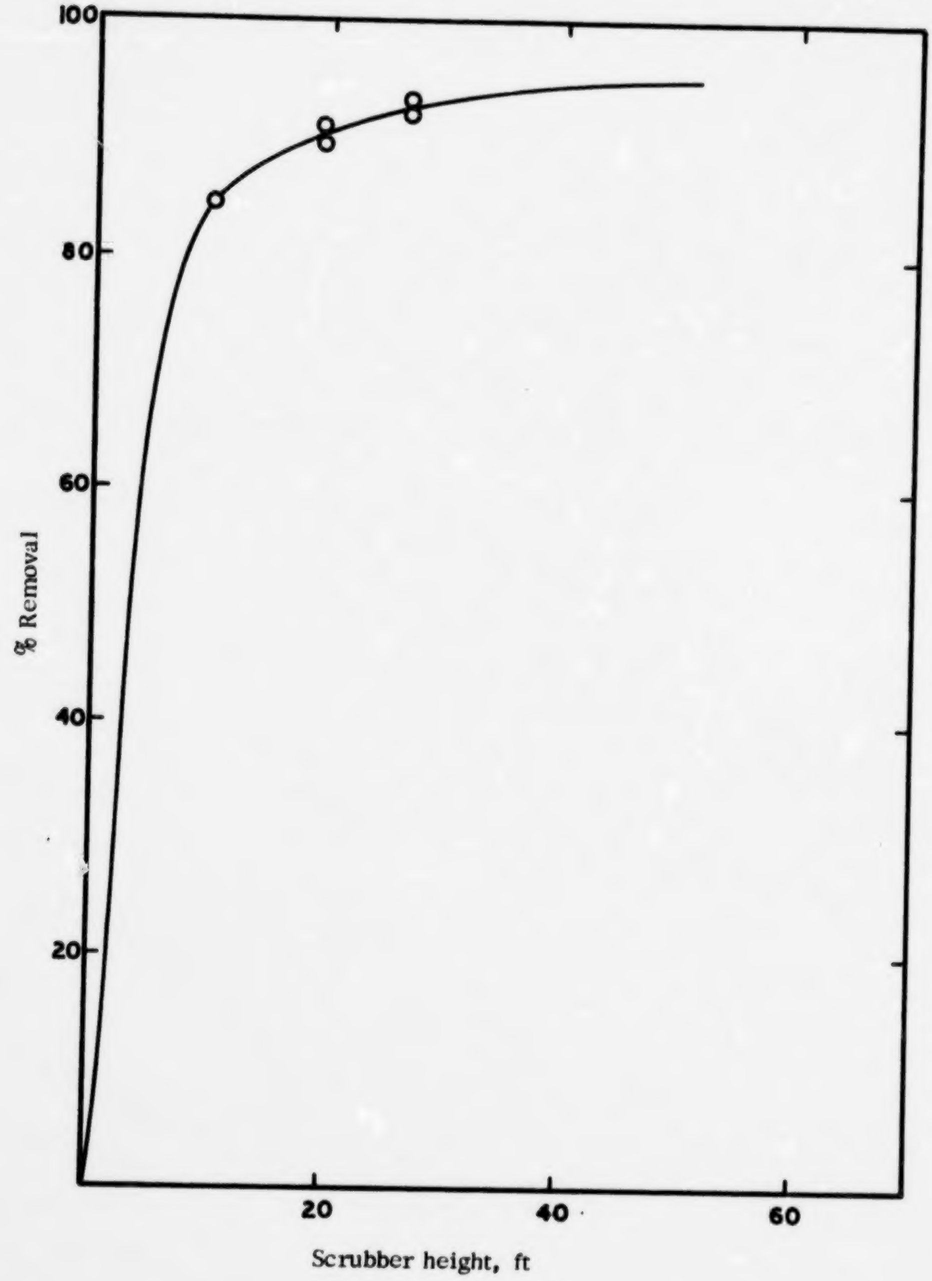

Fig. 37. Extrapolation of data from Runs 85c, 86c, 92c, 93c, and 96c to give scrubber column height for reducing NO_x concentration from 2000 ppm to 100 ppm.

Table XV. Economics of NO_x Scrubbing Plant for 800-MW Power Plant

Tyco Catalytic Chamber Process

Estimated Major Equipment Cost

Basis: 282 lb gas/hr-ft^2 (Miniplant data)

	Item	Use	No.	Size	Cost
1.	Scrubber	NO_x scrubbing	48π	27,000 SCFM 25 ft dia 45 ft high	$ 40,000,000
2.	Packing	For item 1 - scrubber	20,000 ft^3 ea	3-in. Intalox saddles	8,000,000
3.	Stripper	Acid denitrification	3	20 ft dia 30 ft high	750,000
4.	HNO_3 Absorber	HNO_3 production	1	30 ft dia 60 ft high	400,000
5.	Filter	Remove ash from acid	4	-	200,000
6.	Product Storage Tank	Hold HNO_3	2	50,000 gal	50,000
7.	Exhaust fan	Provide differential pressure	4	~ 12-in H_2O	200,000
8.	Pumps	2 stages of pumping to scrubber and stripper	-	Total 50,000 GPM	300,000
					$ 49,900,000

Using Lange Factor of 3.5:
TOTAL INSTALLED COST = $ 175,000,000

Table XVI. Economics of NO_x Scrubbing Plant for 800-MW Power Plant*

Two Catalytic Chamber Process
Basis: 282 [illegible] gas/hr- ft^2 (Miniplant data)
Annual Operating Costs

Catalyst replacement (twice per year)		$ 375,000
Direct labor		200,000
Supervision		60,000
Maintenance	5% of fixed capital	8,750,000
Supplies	15% of maintenance	1,310,000
Utilities		
Power		2,000,000
Water		100,000
Heat (startup only)		150,000
TOTAL DIRECT COST		12,925,000
Payroll burden (20% of direct labor supervision)		52,000
Plant overhead (50% of direct labor, supervision, maintenance,and supplies)		5,160,000
Packing and shipping		20,000
Waste disposal		50,000
TOTAL INDIRECT COST		5,282,000
Depreciation	(10% of fixed capital)	17,500,000
Taxes	(2% of fixed capital)	3,500,000
Insurance	(1% of fixed capital)	1,750,000
TOTAL FIXED COST		$ 22,750,000
TOTAL OPERATING COST (non-regulated)		$ 40,957,000
or 8.5 mil/KWhr		

*330 days operation per year at 75% capacity

Table XVII. Economics of NO_x Scrubbing Plant for 800-MW Power Plant

Tyco Catalytic Chamber Process

Estimated Major Equipment Cost

Basis: 75% of flooding in scrubber

	Item	Use	No.	Size	Cost
1.	Scrubber	NO_x scrubbing	12	120,000 SCFM 25 ft dia 45 ft high	$ 10,000,000
2.	Packing	For item 1 - scrubber	20,000 ft^3 ea	3-in. Intalox saddles	2,000,000
3.	Stripper	Acid denitrification	2	20 ft dia 30 ft high	500,000
4.	HNO_3 Absorber	HNO_3 production	1	30 ft dia 60 ft high	400,000
5.	Filter	Remove ash from acid	4	-	200,000
6.	Product Storage Tank	Hold HNO_3	2	50,000 gal	50,000
7.	Exhaust Fan	Provide differential pressure	2	~12-in H_2O	100,000
8.	Pumps	2 stages of pumping to scrubber and stripper	-	Total 50,000 GPM	150,000
					$ 12,400,000

Using Lange Factor of 3.5:
TOTAL INSTALLED COST = **$ 43,500,000**

Table XVIII. Economics of NO_x Scrubbing Plant for 800-MW Power Plant*

Tyco Catalytic Chamber Process

Annual Operating Costs

Basis: 75% of flooding in scrubber

Catalyst replacement (twice per year)		$ 250,000
Direct labor		150,000
Supervision		50,000
Maintenance	5% of fixed capital	2,170,000
Supplies	15% of maintenance	325,000
Utilities		
Power		750,000
Water		25,000
Heat (startup only)		50,000
TOTAL DIRECT COST		3,760,000
Payroll burden (20% of direct labor supervision)		40,000
Plant overhead (50% of direct labor, supervision, maintenance, and supplies)		1,350,000
Packing and shipping		20,000
Waste disposal		50,000
TOTAL INDIRECT COST		1,460,000
Depreciation	(10% of fixed capital)	4,350,000
Taxes	(2% of fixed capital)	870,000
Insurance	(1% of fixed capital)	435,000
TOTAL FIXED COST		$ 5,655,000
TOTAL OPERATING COST (non-regulated) or 2.3 mil/KWhr		$10,875,000

* 330 days operation per year at 75% capacity

X. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. The gas phase oxidation of SO_2 by NO_2 is too slow to be practical with feed SO_2 levels of 3000 ppm. Residence times of several minutes at 250 to 300 °F would be necessary to achieve 90% oxidation. This would necessitate reactor volumes of several million cubic feet which would be extraordinarily expensive as well as creating enormous technological and logistical problems (e.g., a 5 million cubic foot reactor could be envisioned as 3 miles of 20-ft. diameter ducting).

2. Liquid phase oxidation of SO_2 using 2 wt % $HNSO_5$ in 70% H_2SO_4 can be accomplished in packed towers in residence times of about 15 sec for 90% SO_2 oxidation. The data indicates that the reaction is probably not diffusion controlled, with the limiting step being the liquid phase reaction itself. Techniques for providing a more intimate gas/liquid contact should be able to reduce the residence time down to a workable 10-sec time.

3. The rate of absorption of equimolar quantities of NO and NO_2 in 80% sulfuric acid at 250 °F is not controlled by the individual absorption of the two gases. It appears to be dependent on a gas phase interaction between the two species to form N_2O_3, which is readily absorbed at these conditions. The gas phase reaction is probably slower than the absorption step, in addition to which the equilibrium at these elevated temperatures is shifted towards the unreacted species. These conditions make the absorption from dilute gases very slow compared to absorption in cool acid under the more concentrated conditions of the standard Lead Chamber Process.

4. At 250 to 300 °F, in the presence of less than 0.3% nitrosylsulfuric acid and air, the activated charcoal does not behave as an oxidizing catalyst. Thus, in the stripper/oxidizer state the charcoal probably enters into a reaction with the nitrated sulfuric acid to form NO and CO_2. This is contrary to results obtained at higher nitrosylsulfuric acid concentration and should be verified by further experimentation.

5. The cost of an add-on Catalytic Chamber Plant to remove both SO_2 and NO_2 from power plant stack gas would cost about $413 million for an 800 MW plant if its size were based on miniplant data directly. Its operating cost would be almost 20 mil/KWhr. If the plant were sized using an industry practice level of 75% of flooding in the scrubber, the plant cost could be reduced to $114 million with an annual operating cost of about $27 million or $125/KW and 5.5 mil/KWhr respectively.

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6. If the process were used to remove NO_x only from the stack, the plant cost would be about $175 million and the annual operating cost about $41 million if miniplant data were used directly for scale-up. If 75% of flooding were used here in the scrubbers, the costs would drop to $43.5 million and $10.8 million, respectively. This would be equivalent to $55/KW installed cost and 2.3 mil/KWhr operating cost. Both of these sets of cost estimates bring out the importance of efficient scrubbing operation.

7. The overall conclusion is that the Catalytic Chamber Process at its current level of development is technologically feasible but economically impractical. Major changes must be accomplished in the three primary process stages – SO_2 oxidation reactor, NO_x adsorber, and NO_x stripper/oxidizer – before we have a process of sufficient practicability to justify pilot plant evaluation.

B. Recommendations

In order to bring the Catalytic Chamber Process to a level of development which would justify larger scale evaluation, basic changes must be made in the process. Experimentation to develop these changes should be conducted on each stage separately at the bench scale, rather than the integrated miniplant level, to avoid having equipment problems overshadow basic technological problems. The three primary process stages should be examined:

1. The liquid phase reaction for the oxidation of SO_2 with nitrose should be examined further to see if spray towers or other gas/liquid contractors can be used to reduce the residence time from 15 sec to the order of 5 sec. The current achievement level of 90% reaction in somewhat under 15 sec is not out of the question, but it does require a packed tower having a volume of over 300,000 ft^3, which would be quite costly. Considering that no effort had been made to optimize the contact method in the current contract, it is hard to imagine that considerable improvement in residence time cannot be accomplished.

2. Since the NO and NO_2 do not interact in the gas phase fast enough to permit the use of a high temperature scrubber concept, it may be advantageous to return to the original Lead Chamber Process and use a low temperature scrubber (at about 100°F). The actual NO/NO_2 reaction rate would be slower, but the equilibrium would be shifted to the N_2O_3 side which should make the overall process much faster. The process economics looked poor when the low temperature scrubber was originally examined, but it may be possible to avoid the large heat loss needed to concentrate all the recycle acid by modifying the technique somewhat. One approach would be to withdraw only part of the acid and concentrate it to about 95% acid, withdraw product acid, and then return the remainder to the diluted recycle acid, thus concentrating the recycle stream back to the desired level. In this case there would be no need to recycle the most concentrated acid possible (since this is not the market acid), and it would be advantageous to work at the lowest concentrations, compatible with the process concept. Recent work shows this is about 67% sulfuric acid. A low temperature process which might be practical is shown in Fig. 38.

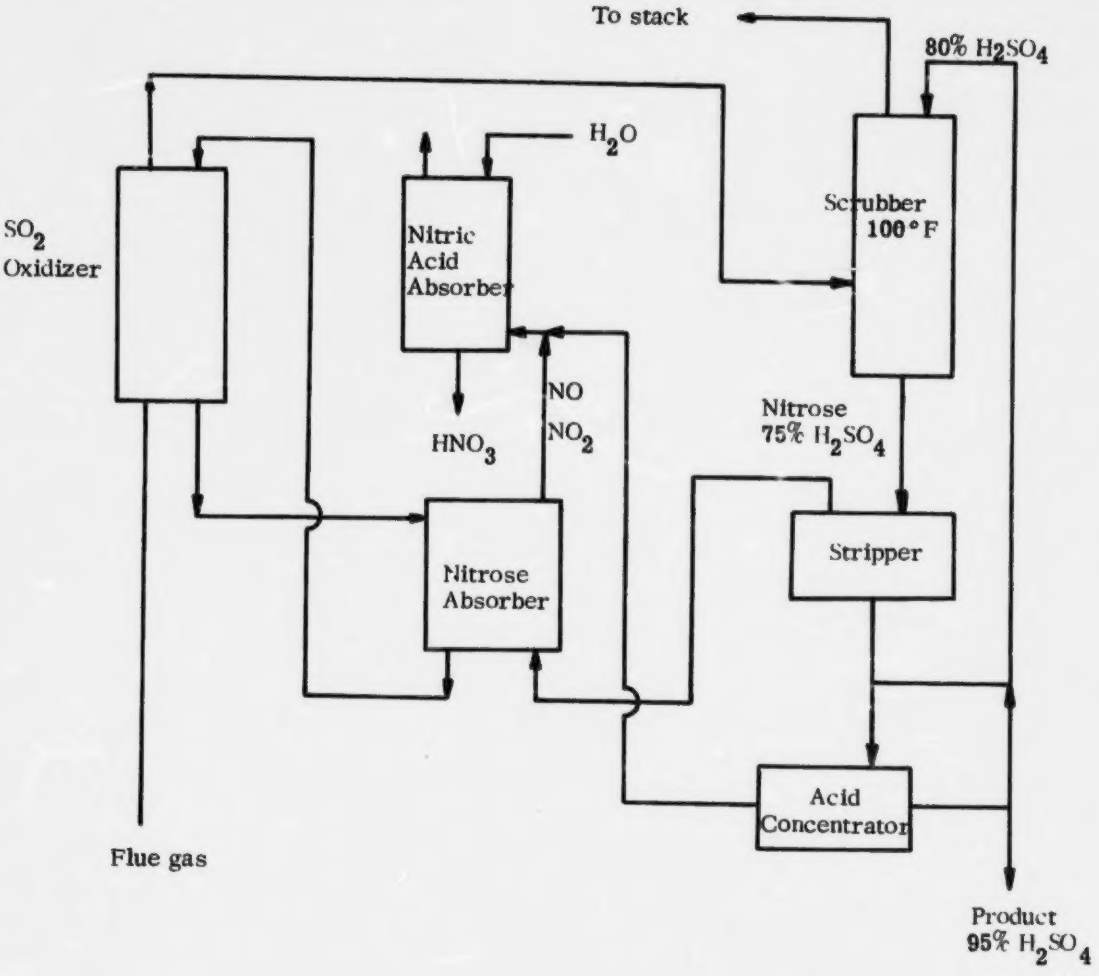
To stack
80% H2SO4
H2O
SO2 Oxidizer
Nitric Acid Absorber
Scrubber 100 °F
NO
NO2
HNO3
Nitrose 75% H2SO4
Stripper
Nitrose Absorber
Acid Concentrator
Flue gas
Product 95% H2SO4

Fig. 38. Catalytic Chamber Process using a low temperature scrubber.

3. More detailed studies should be made of the interaction between dissolved NO_x and activated charcoal to see if there are conditions under which the system can oxidize NO_x rather than reduce it. The data obtained in the contract are not in complete agreement with earlier data obtained at higher nitrosylsulfuric acid concentrations. Prior work also showed that other candidate catalysts denitrated the nitrose, although not as well as the activated charcoal. Further tests should be made with these, including silicon nitride, tungsten carbide, boron carbide, and others (see final report to Contract CPA 70-59).

If work in any of these three areas is not successful, the development of the Catalytic Chamber Process should be discontinued.

XI. ACKNOWLEDGMENTS

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The report was prepared by Arnold H. Gruber and Arthur Walitt of the Corporate Technology Center, Tyco Laboratories. The authors are grateful to the following Tyco personnel for their significant contributions: Dr. David Cogley, Mr. Lewis Gaines and Dr. S. Barry Brummer, along with the pilot plant crew – Edward Broderick, Arthur Chernosky, Irving Frutkoff, Mourad Ghobrial, Gary Hanson, Kamal Ladha, and Vincent Sljaka.

Acknowledgment is also gratefully given to the efforts and contributions of our subcontractor, The Badger Company, and particularly Dr. T.C. Dauphiné, Mr. George A. Randall and Mr. Stephen T. Williams.

In addition, we would also like to acknowledge the helpful discussions with Mr. William Thompson of the Tennessee Valley Authority, Mr. Roger Ramsdell and Mr. Joseph Cunningham of the Consolidated Edison Company of New York, and Mr. Sashil Batra of the New England Power Service Company.

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APPENDIX I. PRELIMINARY ENGINEERING ANALYSIS OF THE TYCO CATALYTIC CHAMBER PROCESS BY BADGER CORPORATION

T. C. Dauphiné of Badger Corp. evaluated the Tyco/Catalytic Chamber Process during the first month of the contract and made recommendations for continued experimentation based on Badger's experience in the operation of pilot-plant facilities as well as the design and construction of full-scale plants. Experiment equipment was modified after consultation with Dr. Dauphiné and George Randall of Badger. The following are excerpts from Dr. Dauphiné's report.

A. Introduction

Badger has been asked to review the data and correlations made available to Tyco and to advise on additional information that may be desirable or necessary for proper definition of the process.

After reviewing the available information and discussing the process conceptions with representatives of both Tyco and Badger, I have the following comments and suggestions.

B. General Background

An essential requirement of the Tyco process is that it must function at high effectiveness over the maximum range of operating rates and conditions of the power plant itself. These requirements thus differ from those of most process plants which are set up for relatively narrow design conditions concerning feed rates and specification, our system must be designed to maintain the effectiveness of the equipment and controls in spite of relatively large variations in feed rate and composition during the daily cycle.

For future experimentation, we have agreed to consider the problems involved with a coal fired plant.

The process problems caused by variation in water concentration in the flue gas must be studied and understood.

A unique feature of the Tyco catalytic process is the high temperature scrubbing of stack gas with 80% sulfuric acid to remove sulfur oxides and nitrogen oxides without absorption of net water into the acid system. Water input into stack gas is subject to change, even at constant firing rate.

C. Reactor (SO_2 Oxidizer)

The reactor mixes a relatively small stream containing NO_2 (from the catalytic stripper) with a large volume of incoming flue gas to oxidize contained SO_2 to SO_3. The reaction involved is:

$$2NO_2 + SO_2 = SO_3 + NO_2 + NO \ .$$

Past laboratory work has indicated that this reaction in small-scale equipment proceeds very rapidly almost to completion. However, as the scale increases, the reaction does not appear to proceed as rapidly.

For commercial scale operation, the problems inherent to very dilute gas phase reactions and problems of mixing large gas streams must be considered and solved.

There also exists a question whether the reaction proceeds rapidly under dry conditions (above the dew point) or depends upon the presence of liquid acid film.

Another question concerns the effect of light in catalyzing the reaction (in miniplant, this reaction has been studied in Pyrex glass equipment).

Experiments now being contemplated will determine the effect on the reaction of additional surface to volume, both wetted and dry.

Other experiments should be made to determine the effect of larger scale on reaction rate.

Temperature (between practical limits anticipated in a plant) should be explored.

Whereas it is desirable to have the input ratio of NO_2 to SO_2 equal to 2:1 so that a mixture of N_2O_3 results, it would be well to explore the effect of ratios different from this to learn what may happen if operating conditions are upset.

For some of these experiments, it may be useful to set up bench equipment separate from the miniplant so that it could run independently from the miniplant to explore a broad range of conditions. Such a setup need not be glass and preferably might be of suitable metal for short time use, and can be useful to get corrosion information.

It would be desirable to know if there is unconverted SO_2 in the exit stream from the reactor, how much SO_3 is present as sulfuric acid mist, the amount of NO_2 and NO in the exit gas, the effect of fly ash upon the reaction, the effect of soot upon the reaction as well as the effect of various amounts of water in the flue gas feed upon the dew point, and the resultant acid condensate which might be formed at high water content levels.

A device which may be useful both for contacting the gases and for dust and mist removal is a "Sirocco" centrifical device which has been used commercially to remove dust and mist from SO_2 gas streams from Pyrites burners.

A check in the literature for materials which might catalyze or poison the reaction is also suggested.

D. High Temperature Scrubber

The high temperature scrubber uses 80% sulfuric acid at about 250 °F to scrub out SO_3,

H_2SO_4, and NO_x from the oxidized flue gas. By controlling the acid inlet temperature, the water vapor leaving with exit flue gas can be controlled to equal that entering, thereby eliminating dilution of acid. Since the amount of water entering per mole of flue gas will change with time, a suitable means for control must be developed.

One alternate would be to shift the temperature of the scrubbing acid to keep the partial pressure of the water vapor in the exit gas equal to that in the entering gas. This might be accomplished with relatively little lag by use of a suitable heater (and cooler).

Another alternate would be to operate the scrubber at a temperature high enough to eliminate the maximum amount of water which might enter the system and to inject water (as required) into the inlet gas to maintain a constant and predetermined partial pressure.

Calculations based on probable changes in water partial pressure will help determine which system might be preferable and what range of variables should be studied now.

This scrubbing equipment must have the ability to operate efficiently at rates well below the maximum design throughout; packed scrubbers are not very satisfactory in this regard and operate efficiently only over a narrow range of throughput, fairly close to the flooding velocity. Channelling of liquid and vapor at lower rates results in poor contact and diminished efficiency. The problem becomes much more severe as the diameter of the equipment becomes larger and the devices to distribute liquid and vapor within the system become more awkward and ineffective.

This may be overcome by using a number of parallel scrubbers, each using a suitable high ratio of height to diameter, and planning to shut off one or more scrubbers from the system as throughput is diminished in order to maintain optimum loadings in the remaining operating columns. In consideration of this, the miniplant work should avoid studying scrubber packed sections which are abnormally short in relation to their diameter; and such ratio of dimensions should not be considered for commercial equipment.

It is important to know accurately whether serious mist removal problems may exist, particularly regarding the flue gas stream from the scrubber. Mist formation in the reactor and its presence in the feed to the scrubber is probably of no concern, since the scrubber itself should be an effective mist remover.

Two approaches appear interesting for eliminating mist. The first is to design the scrubber for low exit gas velocities so mist formation will be minimized and can be removed by a simple "demister" in the top of the column. The second is to provide additional mist eliminators, assuming that it is cheaper to provide this equipment and design the scrubbers for higher exit velocities.

The Sirocco unit for dust and mist removal should also be considered for scrubber exit gas in case mist is a problem; it also provides additional pressure for moving gas.

It is doubtful that operation in laboratory equipment can give any realistic results concerning mist formation. A review of conventional sulfuric acid technology may provide practical information on this point.

The high temperature scrubber has been designed to obtain a given efficiency of NO_x removal, with the NO_2/NO mol ratio being maintained at unity in the entering gas. The effect of different NO_2/NO ratios in the entering gas, and a range of liquid/gas ratios, on the efficiency of the NO_x absorption must be explored over the maximum probable range of variation. It is very important to know how sensitive the efficiency of scrubbing is to variations in these ratios. If both SO_3 and NO_x removal are relatively unaffected by changes in these ratios, it will make control of the commercial unit easy and indicate a high probability of success for this essential part of the Tyco process.

The effect of fly ash upon the scrubber and its operation should be established soon. Fly ash contains a number of metallic impurities, some soluble in the acid, which could affect the chemical reaction in the scrubber. It must also be prevented from physically plugging lines and equipment. A simple test would be to suspend fly ash (or leach it), with 80% sulfuric acid used in scrubbing, and use this in the miniplant to check results against those obtained when using pure 80% sulfuric acid.

Fly ash may be scrubbed out in the acid and at some point would have to be removed from the acid and discarded. The handling properties of typical fly ash in appropriate concentrations in sulfuric acid can be checked on the bench, along with characteristics for drainage, filtration, and centrifuging. Simple experiments could give indications whether fly ash cake has "setting up" or "blinding" properties which would make removal in the plant difficult and expensive. Such experiments should check properties of filtered, neutralized (or alkaline) fly ash as well as for abnormal handling problems.

For a given plant, the gas rate through the scrubber is fixed between certain practical limits. Work in the miniplant should determine the minimum acid scrubbing rate (L/G) needed to attain specified removal of SO_3 and NO_x and performance over a range of higher L/G ratios. These figures are needed for optimizing design of the scrubbing unit and minimizing acid circulation rate.

Another variable planned for miniplant study is the effect of operating temperature upon efficiency over a practical temperature range.

Past runs have been explored at maximum concentrations of N_2O_3 in the inlet gas, and the scrubber has not been able to reduce exit concentration to the desired limit. For assurance in design, it is desirable to know what happens at very dilute concentrations of N_2O_3 approaching design concentration in exit gas. Additional runs in the miniplant are suggested with very low concentrations of N_2O_3 in the gas inlet, other conditions of operation being similar to previous runs.

E. Catalytic Oxidizing Stripper

The heart of the Tyco catalytic process is the catalytic oxidizing stripper, which involves most of the unique and developmental features of the process. The stripper accomplishes two things: first, it contacts the sulfuric acid-nitrose solution from the high temperature scrubber with oxygen (air) over an activated charcoal catalyst, so that $HNSO_5$ is oxidized and hydrated to NO_2 and H_2SO_4; second, it strips NO_2 from the sulfuric acid to produce saleable acid. To date, the most successful operation has been with use of 4 × 10 mesh pellets of No. 256 activated charcoal obtained from Witco.

For the small equipment used to date, this size charcoal packing is appropriate, but would have disadvantages for industrial scale use. First, the mesh size is very small for use in large equipment for countercurrent gas-liquid contacting and may result in high pressure drop and inefficient vapor-liquid contact. Second, the material is mechanically weak and friable, and it may break up and dust in beds deeper than 2 ft. (The manufacturers claim that it has been run in deep beds, and this is usual for decolorization of liquids; but conditions are quite different for its use as a tower packing for countercurrent contact of gas and liquid.)

A search of other available activated charcoals is suggested to try to obtain some of larger size, better mechanical strength, minimum friability and dusting tendencies, and long catalyst life.

Such exploration of their available activated charcoals can use the bench scale single tube screening test already used to select activated carbon from other potential catalysts.

Catalyst life requires continued research for selected catalysts of good initial characteristics. Current studies show negligible loss of activity after passing 78 volume acid/volume catalyst.

It is recommended that future experimentation include determination of the effect of fly ash and soot on catalyst life and activity. In particular, a few simple tests to delineate whether these impurities will impose any new problems or restraints are desirable at an early date.

Past experiments on Witco activated charcoal have shown that scrubber operating temperature (at least 290 °F) and air rate must be maintained at suitable levels to prevent rapid loss of catalyst activity. Obviously, if new alternate catalysts seem worth study, this type of information must be obtained for them. In addition, further experiments at higher temperatures are suggested, with the catalyst used for forthcoming miniplant experiments.

Tests on the oxidizing stripper, using fixed bed charcoal packing, should determine efficiency of contact over this packing, the effect of changing liquid/gas ratios, and the limiting capacity of the packing for acid and air flow (flooding characteristics).

It would be desirable in this equipment, as well as in the scrubber, to determine heat effects; however, the nature and type of equipment available would appear to render this impractical.

Corrosion tests on various metals should also be run in the inlet and outlet from this system. Any effect of dissolved metal upon catalyst reactivity, acid purity, etc., should be noted, as well as corrosion rate.

It may also be interesting to test the stripping of nitrose from sulfuric acid solutions using bench tests and simple equipment, removing the carbon catalyst and having present, instead, contaminants from fly ash and soot. This test could discover if any useful catalytic activity came from their presence.

There may be hazards at some temperature levels in having an oxidizable bed of charcoal in contact with air and an oxidizing acid. Small-scale tests are proposed to determine upper temperature limits which would be safe for operation and to eliminate the possibility of explosive ignition of the carbon bed.

APPENDIX II: MINIPLANT OPERATION

A. Overall Approach

During the scrubber/stripper studies, the operators had to record 27 temperatures, 7 fluid flows, 27 heater control settings (controlling 52 individual heaters), and 11 gas sample concentrations plus 3 complete acid analyses, in addition to keeping track of a variety of process equipment indicators (reservoir levels, column drainage levels, cooling water flows, pump and blower performance, and sample system operation and overall system integrity). Reactor experiments required 8 temperature points, 6 flow rates, and 10 heater control settings as other checks and analyses. (Data sheets showing the information required during the experiments are shown in Tables II-1 through II-4.) Since it was necessary to record a complete set of data on an hourly schedule, a large task for 2 men, it was important that the plant be set up as conveniently as possible. This was accomplished by installing all controls on the upper level of the two-level miniplant. The only tasks that had to be performed on the lower level were the sampling of the acid effluent from the 19-ft scrubber and the enlarged vertical reactor (these, too, could have been taken on the upper level, but there would have been a concentration lag due to the volume in the reservoirs). To further simplify operation, a closed circuit television system was installed to monitor the reservoir levels on the lower plant level, with the level controls being located on the upper level.

B. Gas Sampling System

Gas samples were taken at two points in the reactor system (as shown in Fig. 6) at the inlet and at the outlet. Samples were required at five locations in the scrubber/stripper studies: (1) inlet to 19-ft scrubber, (2) halfway up the 19-ft scrubber, (3) exit from the 19-ft scrubber (feed to 7.5-ft scrubber), (4) exit from the 7.5-ft scrubber, and (5) exit from the strippers. In order to take these samples and analyze them in one system of analytical instrumentation, a manifold system had to be arranged as shown in Fig. II-1.

The system utilized two UV cells for analysis of NO_2 to give accurate analysis at two concentration levels which differed by an order of magnitude, 1% full scale and 10% full scale. These ranges were expected from the scrubber system and stripper system, respectively.

Table II-1. Reactor Data Sheet

DATE: ____________

RUN: ____________

TIME

FLOWS

Infrared Sample
Total Sample
O_2: psig
SCFM
NO: psig
SCFM
Low Air: psig
SCFM
SO_2: psig
SCFM
High Air: SCFM
H_2SO_4
$HNSO_5$ Concentration

TEMPERATURES

Blower Inlet
Inlet Reactor 1
Ultraviolet Analyzer
Acid Feed
Middle Reactor 1
Bottom Reactor 1
Middle Reactor 2
Middle Reactor 3

VOLTAGES

Middle Reactor 1
Bottom Reactor 1
Middle Reactor 2
Bottom Reactor 3
Top Reactor 3
Acid Feed
Top Reactor 2
Inlet to Reactor 1
Bottom Reactor 2
Top Reactor 1

CHECKLIST

Gas Burner
Cooling Water
Drains
Acid Level

OPERATOR

Table II-2. Stripper Data Sheet

Run No. Date Sheet No.

Time

TEMPERATURE

Scrubber 2 Reservoir
Top of Stripper No. 1
" No. 2
" No. 3
Middle of Stripper No. 1
" No. 2
" No. 3
Bottom of Stripper No. 1
" No. 2
" No. 3
Acid Feed: Lower
Middle
Top
Stripper Reservoir

VARIACS

Acid Feed Line
Acid Feed (Res)
Acid Feed Tapes
Stripper Heaters Top
Middle
Bottom
Acid Feed
Top Stripper Tapes

FLOWS

Acid
Air to Stripper

CHECKLIST

Res. Level
Exit Level
Flows

OPERATOR

Table II-3. Scrubber No. 2 Data Sheet

Run No. Date Sheet No.
Time

TEMPERATURES

Main Air Feed
Inlet Air
Acid Feed: Top
Middle
Bottom
Feed Res (Scr 4 Res)
Sample Line

CONTROL VARIACS

Main Air
Gas Feed to Scr Bottom
Gas Feed tc Scr Bottom
Top (1 ft Mantle)
Top (4 ft Mantle)
Top/Middle (4 ft Mantle)
Middle (1 ft Mantle)
Middle/Bottom (4 ft Mantle)
Bottom (4 ft Mantle)
Bottom (1 ft Mantle)
Acid Feed: Immersion Heater
Acid Feed: Tapes
Reservoir

FLOWS

Main Air Meter Reading
Main Air Flow
Acid
NO to Oxidizer Meter Reading
Air to Oxidizer Meter Reading
SO_2 Feed Flow Meter Reading

CHECKLIST

Reservoir Level (TV)
Gas Burner

OPERATOR

129

Table II-4. Scrubber No. 4 Data Sheet

Run No. Date Sheet No.
Time

TEMPERATURES

Acid Feed
Gas Feed: Top
Middle
Bottom
Feed Res (Stripper Res)

CONTROL VARIACS

Feed Res (Stripper Res)
Bottom Mantles
Middle Mantles
Top Mantles
Acid Feed: Top Immersion
Acid Feed: Tapes
Gas Feed
Reservoir

FLOWS

Acid Feed

CHECKLIST

Reservoir
Heater
Column Exit
Leaks
Sample Box
Sample Line

OPERATOR

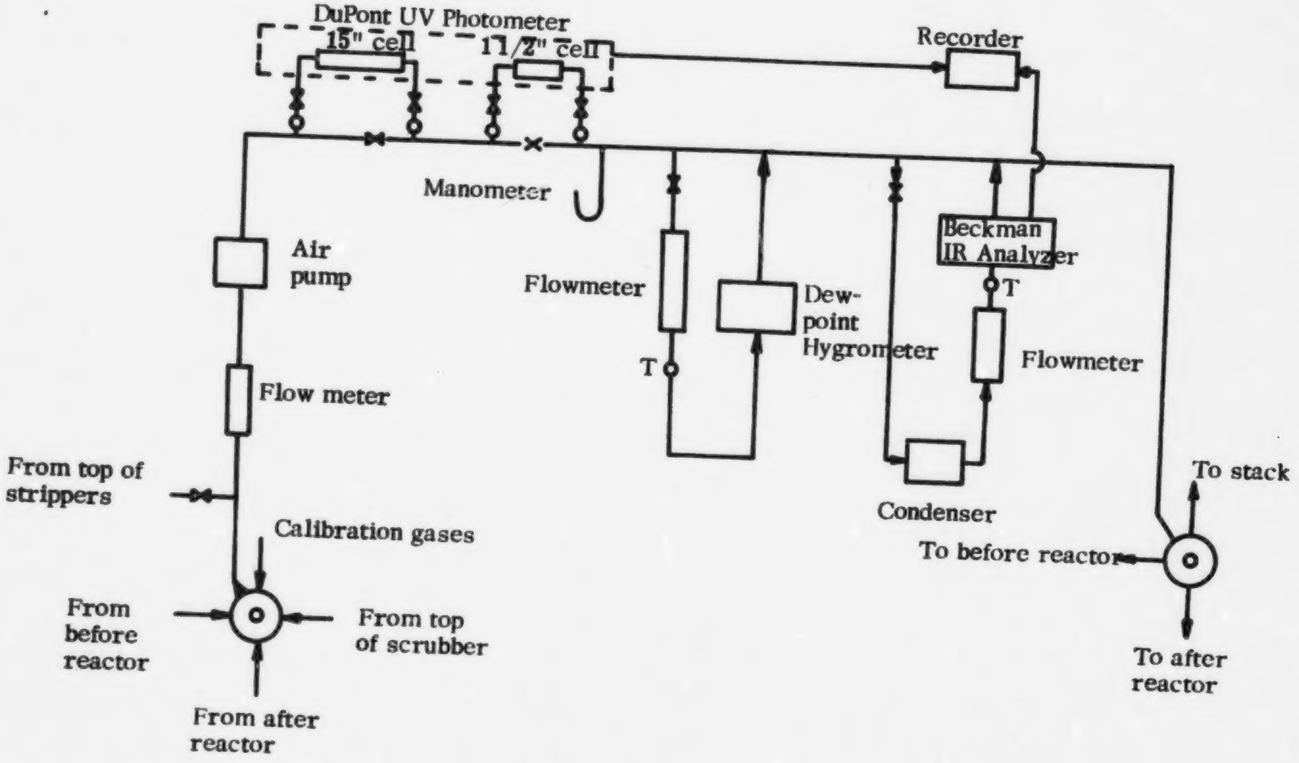
DuPont UV Photometer
15" cell
1 1/2" cell
Recorder
Manometer
Air pump
Flowmeter
Beckman IR Analyzer
T
Dew-point Hygrometer
T
Flowmeter
Flow meter
From top of strippers
Calibration gases
Condenser
To stack
To before reactor
From before reactor
From top of scrubber
To after reactor
From after reactor

Fig. II-1. Flowsheet of gas analysis system.

The gas was pumped out of the miniplant with a small diaphragm pump (about 0.5 SCFM) and fed to the system shown in Fig. II-1. The gas analysis system was set up so that the gas could be returned to the miniplant after it had been analyzed to avoid intermittant fluctuations in process flow levels.

The gas sample was controlled at constant temperature and pressure in the analyzers. This was more important than constant flow rate since the duPont and Beckman instruments both based their analysis on the number of molecules in the path of the radiation beam. A manometer and temperature readout were installed in the sample system near the UV photometer.

The most important feature of the gas sampling system was the control of the condition of the sample. It was necessary to avoid condensation of liquid in the sample lines, a condition which had been known to cause erroneous results in sample analysis. The sample lines were Teflon tubes encased (two or three at a time) in aluminum tubes which were wrapped with heating tapes. In this manner, the gas sample could be kept at about 275 °F while it was outside the miniplant.

If the temperature dropped much below this level, condensation was formed with corroded the stainless steel fittings used in the sample system. The corrosion products tended to block the sample line, resulting in either a high pressure drop (making it difficult to maintain the proper pressure in the system) or a complete blockage of the lines. The system was set up so that an individual line could be isolated and washed with water without removing it from the aluminum tubes. Although the system was workable as used, it was concluded that a more desirable system would utilize individually traced lines. These are more expensive than the system used, but they involve far less maintenance.

Nitric oxide was analyzed with the Beckman infrared analyzer, as shown in Fig. II-1. The primary consideration in this analysis was the removal of water from the gas sample before it reached the analyzer because water interferes with the quantitative analysis of NO in the infrared region of the spectrum. To remove the water, the sample was passed through a cold trap. Experience showed that a large U-tube filled with saddles and immersed in alcohol at −35 °C would drop out most of the water without removing significant amounts of nitrogen oxides. The trap had a tendency to plug up with ice several times a day, but a quick-disconnect system allowed the replacement of the trap in a few minutes and very little time was lost in this type of maintenance. An operator learned to recognize the sudden erratic behavior of the Beckman analyzer output as the symptom of a plugged cold trap.

C. Data-Taking Procedures

As noted above, a complete set of data was taken every hour during a run. A run was not considered to be complete until the essential data were constant for two consecutive sets of readings. The temperatures were taken off the printout of the 24-point recorders and logged onto the data sheets shown earlier. The recorder charts themselves were not retained. Based on the temperature readings, heating rates were adjusted whenever necessary.

Gas sampling was performed continuously, with SO_2, NO_2, and NO being analyzed at each sample point. A gas concentration was considered to be meaningful if the output of the analyzer instrument was constant for 5 to 10 min. Since SO_2 and NO_2 were analyzed on the same instrument, it took several minutes to get a complete analysis at any one sample point.

Acid samples were taken from all required points within a few minutes of each other and analyzed later for acid strength (percent sulfuric acid) and nitrosylsulfuric acid content. In this manner it was hoped that all the data would come close to giving the process condition at one particular time. The acid strength was obtained with a hydrometer (correcting for temperature) and the nitrosylsulfuric acid content determined by titration with potassium permanganate in acid solution:

$$5\ HNSO_5 + H\ MnO_4 + 2H_2O \rightarrow 5H_2SO_4 + HNO_3 + 2Mn(NO_3)_2\ .$$

The acid analysis is quite rapid, except in very dilute solution where it takes as much as 15 min for the color change to become permanent. With $HNSO_5$ concentrations above 0.1%, the titration takes less than 5 min and is quite accurate and reproducible. At lower concentrations the variation between replications can be as much as 5%.

The NO_x content of the acid can be determined by an alternate procedure: the nitrometer. In this case the reducible nitrogen oxides (NO_3^-, NO_2^-) are reduced with mercury to NO gas which is evolved from the solution. The volume of the NO is measured and the original amount of $HNSO_5$ can be calculated if it is assumed that all the NO_x was present as N_2O_3. This is a very accurate method but is very time consuming because it takes a long time for the mercury to react with all the NO_x in the acid solution. In addition, it is not too accurate for very dilute solutions since a small error in reading the colume of NO can make a sizable error in the $HNSO_5$ concentration. All analyses performed during the normal course of miniplant experimentation was done by permanganate titration with occasional checks with the nitrometer on the more concentrated samples.

Fluid flows were recorded once an hour, but were monitored frequently by the miniplant operators. This was accomplished by observing rotameter settings as well as liquid levels in the reservoirs.

D. Shift Operation

Experimentation in the miniplant was performed in continuous "batch" operations. The equipment was run in a continuous fashion for several hours at a time to accomplish the goals of a particular experiment. Then the conditions were changed and another "batch" experiment was performed. This type of testing might have lent itself to an 8-hr day program, except for the fact that it took several hours to bring the plant up to temperature. Because of limitations in the heating equipment and the necessity for slow heating rates on the all-glass piping and columns, it took 4 to 8 hr to achieve thermal steady state.

Due to these requirements and the desire to accomplish as much experimentation as possible during the contract period, the plant operation was conducted on a two or three shift, 5-day week basis. Two operators were present at all times during the three shift work. For the last several weeks of the contract period, the plant was operated for two shifts per day to permit more time during the experimentation for data analysis. The plant was maintained at about 200 °F during the 7-hr period that it was unattended, which cut down the heating time to under 4 hr. This left about 13 hr for experimentation and shutdown. The two shift operation had another advantage in that it provided at least 4 hr every day for equipment maintenance and sample system cleanout. This permitted smoother plant operation during the experimental period.

APPENDIX III. DATA FROM MINIPLANT REACTOR EXPERIMENTATION

Table III-1. Miniplant Reactor Experiment — Irrigation with Nitrose [Three Reactor Columns (1.6 ft^3) Packed with 3/8-in. Intalox Saddles, Acid Feed 4.4% $HNSO_5$ in 70% H_2SO_4 at 20 cc/min]

Run No.	29A	29B	30A	30B	30C	30D	30E
Reactor temperature, °F	250	225	225	225	225	200	200
Gas flow rate (SCFM)	2	2	2	2	2	2	2
Feed SO_2 (ppm)	3550	3550	3450	3450	3450	3450	3450
Feed NO_2 (ppm)	4000	4000	4000	10,400	4000	4000	10,400
Feed NO (ppm)	2325	2325	2325	6000	2325	2325	6000
Feed H_2O (%)	~6	~6	~6	~6	~6	~6	~6
Outlet SO_2 (ppm)	1200	600	650	700	450	150	400
Outlet NO_2 (ppm)	3900	4200	3700	16,400	~5500	5300	11,800
Outlet NO (ppm)	3850	5000	4700	6800	4850	5300	6600
Reactor residence time (sec*)	33.2	34.2	34.2	34.2	34.2	35.8	35.8
SO_2 removal efficiency, %**	70.5	87.4	84.2	94.0	91.3	100	100

---

* Sample line residence time was less than 1 sec using the short UV cell.

** NO_2 interference was taken into account.

Table III-2. Miniplant Experiments — Irrigation with Nitrose [Three Reactor Columns (1.6 ft^3) Packed with 3/8-in. Intalox Saddles*]

Run No.	31				32A			32B		33A			
Reactor temperature (°F)	250	250	250	225	250	250	250	250	250	250	250	250	250
Gas flow rate (SCFM)	2	2	2	2	2	2	2	2	2	2	2	2	2
Gas feed:													
SO_2 (ppm)	3450	3450	3450	3450	3100	3100	3100	2900	2900	3425	3425	3425	3425
NO_2 (ppm)	0	6400	6400	6400	5800	5800	5800	6600	6600	0	5500	5500	0
NO (ppm)	0	2725	2725	2725	2375	2375	2375	2650	2650	0	1700	1700	0
Acid flow rate (cc/min)†	15	15	60	60	25	50	100	135	240	32	32	165	165
Acid feed:													
$HNSO_5$ (%)	4.3	4.3	4.3	4.3	1.12	1.12	1.12	0.63	0.63	1.23	1.23	—	—
H_2SO_4 (%)	70.0	70.0	70.0	70.0	70.8	70.8	70.8	68.7	68.7	78.9	78.9	—	—
Gas effluent:													
SO_2 (ppm)	1900	1100	760	550	1150	850	750	750	600	2900	2150	1700	2650
NO_2 (ppm)	2900	6100	16,900	18,400	4000	4400	4900	8500	13,400	250	3900	3000	—
NO (ppm)	4250	4700	6200	7000	4400	4100	1500	5000	6000	1050	2550	1800	2900
Acid effluent:													
$HNSO_5$ (%)	0.33	0.27	0.78	—	—	—	0.64	—	0.37	—	1.54	1.39	—
H_2SO_4 (%)	66.5	64.4	69.0	—	—	—	71.3	—	64.7	—	76.3	76.3	—
Reactor residence time (sec)	33.2	33.2	33.2	34.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2
Reaction yield (%)	45.0	68.0	78.0	84.0	62.9	72.6	76.5	74.1	79.3	15.5	37.2	50.1	22.9
NO_x material balance error (%) ‡	- 134	10	- 16	—	—	—	30	—	- 42	—	2	6	—

---

* Reactors 1 and 3 were in cocurrent flow rate; reactor 2 was countercurrent.

† Total flow to all 3 reactors.

‡Material balance error = $\frac{NO_x\text{ (in)} - NO_x\text{ (out)}}{NO_x\text{ (in)}} \times 100.$

Table III-2. (Continued)

Run No.	33B			34					35			36		37	
Reactor temperature (°F)	300	300	300	260	260	260	260	260	250	250	250	250	250	250	250
Gas flow rate (SCFM)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Gas feed:															
SO_2 (ppm)	3050	3050	3050	3500	3500	3500	3500	3500	3200	3200	3200	3200	3200	3150	3150
NO_2 (ppm)	6000	6000	6000	7000	0	7000	7000	7000	6500	6500	0	5050	5050	0	0
NO (ppm)	2050	2050	2050	2050	0	2050	2050	2050	2400	2400	0	1775	1775	0	0
Acid flow rate, cc/min†	60	160	160	15	15	57	150	185	60	60	60	15	50	25	80
Acid feed:															
$HNSO_5$ (%)	1.27	1.27	1.27	1.46	1.46	1.46	1.46	1.46	1.13	1.13	1.13	1.13	1.13	0	0
H_2SO_4 (%)	79.6	79.6	79.6	60.0	60.0	60.0	60.0	60.0	53.0	53.0	53.0	71.6§	71.6§	79.8**	79.8**
Gas effluent:															
SO_2 (ppm)	2550	2200	2150	2100	2900	1250	550	425	200	50	600	1200	2200	3150	3150
NO_2 (ppm)	4600	4100	4000	3400	—	4100	6100	6100	—	—	—	—	—	—	—
NO (ppm)	3100	3075	3350	2900	—	4700	6000	6600	—	—	—	—	—	—	—
Acid effluent:															
$HNSO_5$ (%)	—	—	1.03	—	—	—	—	—	—	—	—	—	—	—	—
H_2SO_4 (%)	—	—	77.3	—	—	—	—	—	—	—	—	—	—	—	—
Reactor residence time (sec)	29.9	29.9	29.9	32.9	32.9	32.9	32.9	32.9	33.2	33.2	33.2	33.2	33.2	33.2	33.2
Reaction yield (%)	16.4	27.9	29.5	40.0	17.1	64.4	84.3	87.8	93.8	98.4	81.3	62.0	31.7	0	0
NO_x material balance error (%) ‡	—	—	14	—	—	—	—	—	—	—	—	—	—	—	—

---

* Reactors 1 and 3 were in cocurrent flow rate, reactor 2 was countercurrent.

† Total flow to all 3 reactors.

‡ Material balance error = $\frac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)} \times 100.$

§ 2.24% HNO_3 added.

** 2.95% HNO_3 added.

Table III-2. (Continued)

Run No.	38	38A				39			40			
Reactor temperature (°F)	250	250	250	250	250	250	250	250	250	250	250	250
Gas flow rate (SCFM)	2	2	2	2	2	2	2	2	2	2	2	2
Gas feed:												
SO_2 (ppm)	3100	2950	2950	2950	2950	3200	3200	3200	3200	3200	3200	3200
NO_2 (ppm)	4700	5500	5500	5500	0	5500	5500	5500	6100	6100	6100	0
NO (ppm)	1225	1775	1775	1775	0	1900	1900	1900	2100	2100	2100	0
Acid flow rate (cc/min)	20	60	140	260	260	33	50	181	70	140	260	260
Acid feed:												
$HNSO_5$ (%)	1.17	1.04	1.04	1.04	1.04	1.26	1.26	1.26	2.06	2.06	2.06	2.06
H_2SO_4 (%)	71.2§	70.7	70.7	70.7	70.7	80.4	80.4	80.4	79.3	79.3	79.3	79.3
Gas effluent:												
SO_2 (ppm)	1400	1150	400	150	500	2000	2250	1850	1100	950	500	1150
NO_2 (ppm)	3900	4200	6100	6800	3600	—	—	—	3100	4000	2500	300
NO (ppm)	2600	2900	4400	4625	4400	—	—	—	2100	3100	2325	4250
Acid effluent:												
$HNSO_5$ (%)	1.58	—	—	—	—	—	—	—	—	—	—	—
H_2SO_4 (%)	74.9	—	—	—	—	—	—	—	—	—	—	—
Reactor residence time (sec)	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2
Reaction yield (%)	54.8	62.7	86.4	94.9	83.1	37.5	29.5	42.2	65.6	70.3	84.4	64.0
‡NO_x material balance error (%)	- 14	—	—	—	—	—	—	—	—	—	—	—

---

* Reactors 1 and 3 were in cocurrent flow rate, reactor 2 was countercurrent.

† Total flow to all 3 reactors.

‡ Material balance error = $\dfrac{NO_x\,(in) - NO_x\,(out)}{NO_x\,(in)} \times 100.$

§ 0.45% HNO_3 present.

Table III-2. (Continued)

Run No.	41						42		43		44				
Reactor temperature (°F)	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250
Gas flow rate (SCFM)	4	4	4	4	4	4	4	4	8	8	4	4	4	4	4
Gas feed:															
SO_2 (ppm)	3850	3850	3850	3850	3850	3850	3150	3150	3050	3050	3200	3200	3200	3200	3200
NO_2 (ppm)	7500	7500	7500	7500	7500	0	5600	5600	6100	6100	6500	0	6500	6500	6500
NO (ppm)	2900	2900	2900	2900	2900	0	1950	1950	2325	2325	2175	0	2175	2175	2175
Acid flow rate (cc/min) †	55	55	120	280	500	500	120	255	110	280	64	64	122	257	484
Acid feed:															
$HNSO_5$ (%)	1.0	1.0	1.0	1.0	1.0	1.0	0.91	0.91	1.06	1.06	0.53	0.53	0.53	0.53	0.53
H_2SO_4 (%)	71.1	71.1	71.1	71.1	71.1	71.1	75.8	75.8	69.7	69.7	70.0	70.0	70.0	70.0	70.0
Gas effluent:															
SO_2 (ppm)	3000	2275	1175	550	0	375	2150	1850	2050	1400	1775	2825	1400	1225	1075
NO_2 (ppm)	900	5800	7500	8500	7500	5500	—	—	—	—	4350	200	4600	5000	4725
NO (ppm)	3625	4400	5400	6000	5600	5900	—	—	—	—	3225	950	3500	3850	3750
Acid effluent:															
$HNSO_5$ (%)	—	0.59	0.96	0.70	0.86	—	—	—	—	—	0.45	—	0.45	0.42	0.39
H_2SO_4 (%)	—	72.9	72.6	71.2	69.6	—	—	—	—	—	70.0	—	71.0	70.0	70.6
Reactor residence time (sec)	16.6	16.6	16.6	16.6	16.6	16.6	16.6	16.6	8.3	8.3	16.6	16.6	16.6	16.6	16.6
Reaction yield (%)	22.1	40.7	69.6	85.5	100	90.3	31.8	41.5	32.8	54.1	44.6	11.7	56.3	62.0	66.6
NO_x material balance error (%) ‡	—	6	-18	-11	-4	—	—	—	—	—	13	—	9	5	13

---

* Reactors 1 and 3 were in cocurrent flow rate, reactor 2 was countercurrent.

† Total flow to all 3 reactors.

‡ Material balance error = $\frac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)} \times 100.$

Table III-2. (Continued)

Run No.	45	46§							47§			
Reactor temperature (°F)	250	250	250	250	250	250	250	250	250	250	250	250
Gas flow rate (SCFM)	6	2	2	2	2	2	2	2	4	4	4	4
Gas feed:												
SO_2 (ppm)	—	3300	3300	3300	3300	3300	3300	3300	3250	3250	3250	3250
NO_2 (ppm)	—	6400	6400	6400	6400	6400	6400	0	6200	6200	6200	6200
NO (ppm)	—	1800	1800	1800	1800	1800	1800	0	1950	1950	1950	1950
Acid flow rate (cc/min)†	—	15	42	57	89	134	248	248	29	82	179	220
Acid feed:												
$HNSO_5$ (%)	—	1.12	1.12	1.12	1.12	1.12	1.12	1.12	0.96	0.96	0.96	0.96
H_2SO_4 (%)	—	71.5	71.5	71.5	71.5	71.5	71.5	71.5	73.4	73.4	73.4	73.4
Gas effluent:												
SO_2 (ppm)	—	2550	2300	2400	1500	1400	900	975	2925	2600	2200	1950
NO_2 (ppm)	—	6100	6700	6700	7700	8600	8125	6200	4950	5000	4600	4900
NO (ppm)	—	3850	4025	3975	4625	5000	4025	4850	3500	3550	4000	4025
Acid effluent:												
$HNSO_5$ (%)	—	1.64	1.85	2.1	1.36	0.81	0.65	—	—	0.62	0.67	0.63
H_2SO_4 (%)	—	72.8	80.4	74.9	77.9	67.7	72.9	—	—	—	74.4	73.7
Reactor residence time (sec)	—	24.9	33.2	33.2	33.2	33.2	33.2	33.2	16.6	16.6	16.6	16.6
Reaction yield (%)	—	$\frac{22.7}{63.6}$ **	$\frac{30.3}{66.7}$	$\frac{27.7}{71.0}$	$\frac{54.6}{78.0}$	$\frac{57.6}{89.4}$	$\frac{72.9}{100}$	$\frac{70.6}{96.0}$	$\frac{10.0}{26.0}$ **	$\frac{20.0}{26.0}$	$\frac{32.4}{33.0}$	$\frac{40.0}{50.8}$
NO_x material balance error (%) ‡	—	-23	-38	-47	-39	-22	9	—	—	3	7	8

---

* Reactors 1 and 3 were in cocurrent flow rate; reactor 2 was countercurrent.

† Total flow to all 3 reactors.

‡ Material balance error = $\frac{NO_x\text{ (in)} - NO_x\text{ (out)}}{NO_x\text{ (in)}} \times 100.$

§ One reactor: cocurrent operation — effluent data for one column only.

** The yield values represent SO_2 removal rates after one irrigated column (above the slash line) and after the third reactor; i.e., one irrigated reactor and unirrigated, but wetted packed columns (below the slash line).

Table III-2. (Continued)

Run No.	48§				49§		
Reactor temperature (°F)	250	250	250	250	250	250	250
Gas flow rate (SCFM)	2	2	2	2	4	4	4
Gas feed:							
SO_2 (ppm)	3050	3050	3050	3050	3450	3450	3450
NO_2 (ppm)	5850	5850	5850	5850	5900	5900	5900
NO (ppm)	1950	1950	1950	1950	2200	2200	2200
Acid flow rate (cc/min) †	29	59	136	204	30	180	350
Acid feed:							
$HNSO_5$ (%)	0.95	0.95	0.95	0.95	0.95	0.95	0.95
H_2SO_4 (%)	72.7	72.7	72.7	72.7	72.7	72.7	72.7
Gas effluent:							
SO_2 (ppm)	2175	1550	1275	1200	—	—	—
NO_2 (ppm)	4600	5200	5300	5600	5500	4500	4400
NO (ppm)	3750	4700	5050	5100	3350	3900	2650
Acid effluent:							
$HNSO_5$ (%)	0.54	0.56	0.79	0.89	0.71	0.67	0.69
H_2SO_4 (%)	75.5	74.7	73.9	73.9	71.0	70.9	71.2
Reactor residence time (sec)	33.2	33.2	33.2	33.2	16.6	16.6	16.6
Reaction yield (%)	28.7	49.0	58.5	60.0	9.9	27.3	31.7
NO_x material balance error (%) ‡	1	−8	−10	−13	−6	8	20

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* Reactors 1 and 3 were in cocurrent flow rate; reactor 2 was countercurrent.

† Total flow to all 3 reactors.

‡ Material balance error = $\frac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)} \times 100.$

§ One reactor was countercurrent.

Table III-3. Miniplant Reactor Experiments — Irrigation with Nitrose (One 15-ft Reactor in Countercurrent Operation Reactor Packed with 3/8-in. Intalox Saddles)

Run No.	52		52A		53	54				55†	56A
Reactor temperature (°F)	210	208	218	222	224	219	232	227	227	~250	250
Gas flow rate (SCFM)	2	2	2	2	4	2	2	2	2	2	2
Gas feed:											
SO_2 (ppm)	3500	3500	3100	3100	2875	2900	2900	2900	2900	3000	3300
NO_2 (ppm)	5800	5800	6250	6250	5100	5900	5900	5900	5900	6150	5900
NO (ppm)	1900	1900	1775	1775	2150	2550	2550	2550	2550	1675	1050
Acid flow rate (cc/min)	330	330	320	320	100	20	25	35	35	230	180
Acid feed:											
$HNSO_5$ (%)	1.9	1.8	1.10	0.78	0.8	1.29	1.26	1.53	1.53	0.06	2.13
H_2SO_4 (%)	76.0	72.0	69.4	72.1	71.3	73.1	73.1	73.1	73.1	68.1	69.8
Gas effluent:											
SO_2 (ppm)	850	750	750	550	1350	100	300	100	325	~1700	1850
NO_2 (ppm)	7200	5100	10,800	4350	4300	4000	4650	5600	5700	4100	18,000
NO (ppm)	4700	3850	5010	4100	4200	3750	4200	4250	4025	3550	3100
Acid effluent:											
$HNSO_5$ (%)	1.2	1.0	0.77	0.47	0.39	0.81	0.89	0.93	0.93	0.14	0.20
H_2SO_4 (%)	76.3	72.3	69.5	72.4	71.3	72.3	72.9	73.0	73.0	68.4	70.4
Reactor residence time (sec)	29	29	28	28	14	28	28	28	28	27	27
Reaction yield (%)	76.0	78.5	75.9	79.0	51.7	98.5	89.7	96.4	88.8	42.5	43.9
NO_x material balance error (%)	+21	+33	−7	+23	−1	+12	+1	−2	−1	−10	+18

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*Material balance error = $\frac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)}$.

†Unstable system.

Table III-3. (Continued)

Run No.	56B	56C	57A	57A'		57B		57B'	57C	58		59
Reactor temperature (°F)	217	201	201	200	200	225	226	225	250	220	220	225
Gas flow rate (SCFM)	2	2	2	2	2	2	2	2	2	2	2	4
Gas feed:												
SO_2 (ppm)	3300	3300	3000	3250	3250	3250	3250	3300	2675†	2575†	2625†	3200†
NO_2 (ppm)	5900	5900	5875	0	6000	6000	6000	6100	6200	7500	7500	6400
NO (ppm)	1050	1050	2200	0	1800	1800	1800	2600	2400	3175	3175	2150
Acid flow rate (cc/min)	200	210	45	35	35	50	35	35	40	30	30	35
Acid feed:												
$HNSO_5$ (%)	1.66	1.86	1.65	2.16	2.16	2.69	—	2.55	2.40	1.01	1.19	0.92
H_2SO_4 (%)	69.8	69.4	67.8	70.1	70.1	69.5	—	71.6	70.0	72.4	72.6	72.0
Gas effluent:												
SO_2 (ppm)	1000	700	1100‡	2300	500	800	875	250	1450†	150†	250†	450†
NO_2 (ppm)	15,000	12,000	15,000	—	4500	6000	8000	2400	8600	7500	7500	3800
NO (ppm)	2900	2900	~6000	5000	5000	5050	5050	6000	7000	2550	2550	2800
Acid effluent:												
$HNSO_5$ (%)	0.26	0.23	0.16	0.25	0.25	0.55	—	0.21	0.82	0.62	0.59	0.52
H_2SO_4 (%)	69.8	69.8	68.9	67.3	67.3	73.6	—	70.4	76.6	72.7	72.7	72.3
Reactor residence time (sec)	28	29	29	29	29	28	28	28	27	28	28	14
Reaction yield (%)	66.6	78.8	63.2	29.3	84.6	75.5	74.4	92.5	45.9	94.3	90.5	79.6
NO_x material balance error (%)	+ 18	+ 38	−76	—	+ 16	+ 18	—	+ 35	−25	+ 10	+ 13	+ 25

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*Material balance error = $\dfrac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)}$.

†Corrected for zero error.

‡Instruments in error.

Table III-4. Miniplant Reactor Experiments — Irrigation with Nitrose (One 15-ft Reactor in Cocurrent Operation Reactor Packed with 3/8-in. Intalox Saddles)

Run No.	60			61	62A	62B
Reactor temperature (°F)	228	228	213	221	222‡	222‡
Gas flow rate (SCFM)	4	4	4	4	4	4
Gas feed:						
SO_2 (ppm)	2450†	2450†	3200†	3300†	2875†	2575†
NO_2 (ppm)	6000	6000	6400	6300	6000	6160
NO (ppm)	2850	2850	1800	3025	1000	2250
Acid flow rate (cc/min)	205	200	200	30	305	380
Acid feed:						
$HNSO_5$ (%)	1.3	1.5	1.93	1.83	1.29	2.65
H_2SO_4 (%)	71.0	71.5	72.2	70.3	70.4	71.3
Gas effluent:						
SO_2 (ppm)	400†	400†	250†	800†	350†	150†
NO_2 (ppm)	—	4100	7100	4900	6600	12,500
NO (ppm)	3550	3425	~5500	5000	2375	11,400
Acid effluent:						
$HNSO_5$ (%)	0.8	1.08	0.61	0.31	0.78	1.27
H_2SO_4 (%)	72.1	71.0	71.2	70.4	70.7	72.3
Reactor residence time (sec)	14	14	14	14	14	14
Reaction yield (%)	83.8	83.7	92.4	75.7	87.7	94.3
NO_x material balance error (%)	—	+ 21	+ 15	+ 6	+ 22	-3

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*Material balance error = $\frac{NO_x\ (in) - NO_x\ (out)}{NO_x\ (in)}$.

†Corrected for zero error.

‡Reactor temperature: top - 195 °F, middle - 234 °F, bottom - 230 °F.

APPENDIX IV. DATA FROM SCRUBBER/STRIPPER EXPERIMENTS

Table IV-1. Scrubber/Stripper Data

Run No.			67					68 (Repeat of 67)									
			A	B	C	D	E	A	B	C*	D	E	F	G	H	I	J
T_{NA}		°F	240/ 300	230/ 300	230/ 300	235/ 300	265/ 300	145/ 205	140/ 285	180/ 285	200/ 285	245/ 280	245/ 280	250/ 278	250/ 278	245/ 275	245/ 275
T_{HD}		°F	240/ 290	240/ 300	250/ 310	250/ 315	240/ 310	150/ 200	160/ 190	170/ 220	200/ 220	200/ 220	200/ 220	230	230	235	235
$Q_{Flue\ Gas}$		SCFM	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	erratic
Q_{Acid}		GPM	0.22	0.22	0.22	0.22	0.22	0.24	0.24	0.22	0.22	0.22	0.22	0.2	0.2	0.2	0.2
Q_{Air}		SCFM															
$[C_{HNSO_5}]$	1	wt %	—	0.08	0.11	0.22	—	—	—	—	0.17	0.15	—	0.23	—	0.16	0.59
	2	"	—	0.34	0.37	0.76	—	—	—	—	0.25	0.23	—	0.29	—	0.27	0.35
	3	"	—	0.08	0.09	0.18	—	—	0.30	—	0.08	0.06	—	0.14	—	0.06	0.18
$[C_{H_2SO_4}]$	1	wt %	—	—	76.6	—	—	—	—	—	76.0	76.0	—	76.0	—	76.3	75.5
	2	"	—	—	78.0	—	—	—	—	—	76.0	76.0	—	76.0	—	76.3	82.1
	3**	"	—	—	77.4	—	—	—	74.7	—	76.0	76.0	—	76.0	—	76.3	75.7
$[C_{NO_2}]$	Flue Gas	ppm	3900	4150	3450	3600	3050	3300	3900	3200	3150	3300	2300	3100	3300	3450	3450
	1	"	—	875	400	500	0	800	375	3175	2100	2000	1800	2325	2050	1450	—
	2	"	3400	1000	400	0	350	2500	—	5050	2900	3175	—	3025	—	2000	5050
	3	"	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NO_x Scrubbing Efficiency			—	71.1	73.2	68.3	66.4	79.0	90.0	21.0	39.6	58.8	51.8	40.6	36.0	52.7	61.0
$[C_{NO}]$	Flue Gas	ppm	1300	2600	2375	2735	3025	2900	2950	4100	3975	4700	4325	4100	3500	3625	3350
	1	"	950	1075	1150	1500	2050	500	300	2600	2200	1300	1400	1900	2300	1900	—
	2	"	erratic	1225	1400	1900	1850	500	—	3500	2400	1950	—	2200	—	2300	5100
	3	"	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NO_x Matl. Bal. Error		%	—	8.9	-1.9	-51.8	—	—	—	—	2.3	22.9	—	9.3	—	9.1	—
$[C_{H_2O}]$	Flue Gas***		~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~6
	Air		~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1

Key to Effluent Streams: 1 - NO_x scrubber 4; 2 - NO_x scrubber 2; 3 - stripper.

*Plant shut down after 68E and started up again. Sample line problems (this is where the Teflon sample lines fused and gave us difficulty).

**No SO_2 was fed to the scrubbers during Runs 68-72.

***No H_2O analyses were made on the scrubber and stripper effluent gases.

Table IV-1. (Continued)

Run No.			70 (2 Strippers)							70 Repeat (2 Strippers)				71		
			A	B	C	D	E	F	G	H	J	K	L**	A†	B†	C‡
T_{NA}		°F	230/260	235/265	235/265	240/270	255/305	255/305	260/280	245/260	170/265	175/260	240/260	~230/250	170/255	170/255
T_{HD}		°F	250/270	255/275	255/275	240/295	245/295	245/295	245/295	~260	330/280	230/280	230/285	~240	190/240	225/260
$Q_{Flue\ Gas}$		SCFM	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Q_{Acid}		GPM	0.19	0.16	0.16	0.17	0.14	0.14	0.16	0.16	0.18	—	—	0.18	0.18	0.16
Q_{Air}		SCFM							2.25							
$[C_{HNSO_5}]$	1	wt %	0.03	0.03	0.08	0.42	—	0.29	0.31	—	0.02	—	—	—	0.07*	0.07*
	2	"	0.51	0.51	1.06	1.13	—	0.80	0.81	—	0.45*	—	—	—	0.25*	0.38*
	3	"	—	—	—	0.21	—	—	0.31	—	0.01	—	—	—	0.02*	0.05*
$[C_{H_2SO_4}]$	1	wt %	78.2	78.2	78.4	77.9	—	77.3	77.5	—	—	—	80.4	—	77.0	77.2
	2	"	78.0	78.0	78.6	78.7	—	78.0	78.0	—	—	—	79.3	—	77.0	77.2
	3	"	—	—	—	78.2	—	78.7	78.9	—	—	—	78.9	—	77.0	77.2
$[C_{NO_2}]$	Flue Gas	ppm	2800	2900	2950	3500	3800	3350	3650	3100	3050	3300	3600	2900	3000	3000
	1	"	400	550	700	1200	1125	1300	1300	300	400	400	1200	1900	2300	2000
	2	"	700	900	1000	1350	1200	1400	1300	1600	600	1000	1700	2700	2900	2700
	3	"	—	—	—	—	—	—	—	—	—	1400	—	—	—	—
NO_x Scrubbing Efficiency			27.5	76.4	77.4	71.3	72.4	65.8	67.9	74.5	79.0	82.0	58.0	51.4	36.0	50.6
$[C_{NO}]$	Flue Gas	ppm	3650	3350	3425	3175	3425	3350	3350	3750	3350	3350	3300	2550	2150	2850
	1	"	1050	925	750	750	875	1000	950	1400	950	800	1400	750	1000	925
	2	"	950	875	875	850	950	1100	1075	2250	925	1100	1725	950	1025	1050
	3	"	—	—	—	—	—	—	—	—	—	1800	—	—	—	—
NO_x Matl. Bal. Error		%	-43.7	—	—	-82.8	—	—	-15.4	—	-20.5	—	—	—	-27.0	-20.0
$[C_{H_2O}]$	Flue Gas		~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~6	~1	~1	~6
	Air		~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1	~1

Key to Effluent Streams: 1 - NO_x scrubber 4; 2 - NO_x scrubber 2; 3 - stripper.

*Using acid blank for analysis.
**Instrumentation problems.
†Dry gas feed.
‡Wet gas feed.

Table IV-1. (Continued)

Run No.			74								75			
			A	B	C	D	E	F	G	H	A	B	C	D
Relative Time		hr.	0	0.5	1.0	2.25	3.75	5.25	7.25	8.25	0	0.5	1.5	3.0
T_{NA}		°F	190/290	190/290	195/280	195/280	195/280	190/250	195/250	195/250	210/290	210/290	210/290	215/275
T_2 - Avg.		°F	252	252	252	252	252	227	227	231	272	272	272	252
T_4 - Avg.		°F	210	217	217	217	207	207	213	213	253	255	255	232
T_{HD}		°F	230/255	230/255	240/260	240/260	240/260	245/255	245/250	245/250	245/260	245/260	245/260	255/265
T_{HD} - Avg.		°F	247	247	250	250	250	250	250	250	255	254	254	258
$Q_{Flue Gas}$*		SCFM	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
Q_{Acid}		GPM	0.28	0.28	0.27	0.28	0.28	0.28	0.26	0.31	0.25	0.25	0.25	0.25
Q_{Air}**		SCFM	2.55	2.55	2.55	3.6	3.6	3.6	3.6	3.6	3.4	3.4	3.4	1.9
$[C_{HNSO_5}]$	1	wt %	-	-	-	0.02	-	.008	-	.007	0.05	.049	.049	.070
	2	"	-	-	-	0.06	-	.015	-	.008	.256	.258	.258	.320
	3	"	-	-	-	0.03	-	.019	-	.005	.010	.015	.015	.008
$[C_{H_2SO_4}]$	1	wt %	-	-	-	69.8	-	78.0	-	78.0	79.2	78.2	78.2	77.9
	2	"	-	-	-	69.8	-	77.7	-	77.3	77.2	78.2	78.2	77.9
	3	"	-	-	-	69.8	-	77.3	-	77.9	79.2	78.2	78.2	78.2
$[C_{NO_2}]$	Flue Gas	ppm	500	500	450	575	580	470	-	645	3100	3100	3100	3100
	1	"	-	-	-	110	70	10	30	-	1000	1000	1000	1000
	2	"	50	55	75	170	120	70	-	40	1300	1300	1300	1250
	3	"	-	-	-	20	-	-	0	-	1350	1300	1450	5100
	4	"	-	-	-	-	-	-	-	-	-	-	-	-
$[C_{NO}]$	Flue Gas	ppm	1100	1000	725	450	300	300	-	450	3725	3725	3760	3850
	1	"	-	-	-	175	150	110	100	-	650	675	575	500
	2	"	550	325	375	160	100	100	-	75	1000	1050	950	775
	3	"	-	-	-	150	-	-	110	-	5800	6000	5900	8200
	4	"	-	-	-	-	-	-	-	-	-	-	-	-
NO_x Scrubbing Efficiency	10.0 ft.	%	-	-	-	-	-	-	-	-	-	-	-	-
	19.0 ft.	"	-	-	-	-	-	-	-	-	-	-	-	-
	26.5 ft.	"	-	-	-	71.0	75.0	84.5	83.2	89.0	76.0	75.5	77.0	78.4
NO_x Matl. Bal. Error		%	-	-	-	10.0	-	-	-	-	6.3	~6	~6	-2.2

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*The flue gas contains ~ 6% H_2O.

**The air fed to the strippers contains ~1% H_2O.

Table IV-1. (Continued)

Run No.			72		
			A	B	C
T_{NA}		°F	180/ 260	180/ 265	180/ 260
T_{HD}		°F	250/ 270	250/ 270	255/ 270
$Q_{Flue\ Gas}$		SCFM	4	4	4
Q_{Acid}		GPM	0.17	0.16	0.18
Q_{Air}		SCFM			
$[C_{HNSO_5}]$	1	wt %	0.30	0.30	0.70
	2	"	0.64	0.60	0.76
	3	"	0.21	0.30	0.30
$[C_{H_2SO_4}]$	1	wt %	77.5	76.6	77.3
	2	"	71.2	77.7	77.3
	3	"	77.7	77.5	77.3
$[C_{NO_2}]$	Flue Gas	ppm	3050	3100	3100
	1	"	2250	2150	2300
	2	"	2300	2250	2400
	3	"	—	—	—
NO_x Scrubbing Efficiency			45.4	48.4	44.8
$[C_{NO}]$	Flue Gas	ppm	3050	3100	~3400
	1	"	1075	1050	1150
	2	"	725	825	775
	3	"	—	—	—
NO_x Matl. Bal. Error		%	-47.3	-16.4	-44.4
$[C_{H_2O}]$	Flue Gas		~6	~6	~6
	Air		~1	~1	~1

Key to Effluent Streams: 1 - NO_x scrubber 4; 2 - NO_x scrubber 2; 3 - stripper.

Table IV-1. (Continued)

			76				77*	78**	
Run No.			A	B	C	D		A	B
Relative Time		hr.	0	1.0	4.75	5.25	-	0	3.0
T_{NA}		°F	220/ 275	230/ 280	215/ 260	225/ 265	125/ 260	220/ 270	220/ 270
T_2 - Avg.		°F	264	264	231	234	244	264	259
T_4 - Avg.		°F	242	242	252	231	243	235	237
T_{HD}		°F	240/ 260	250/ 260	250/ 260	250/ 260	240/ 255	240/ 260	240/ 260
T_{HD} - Avg.		°F	251	251	253	252	251	251	251
$Q_{Flue\ Gas}$		SCFM	5.6	5.6	5.6	5.6	5.6	5.6	5.6
Q_{Acid}		GPM	0.26	0.27	0.27	0.28	0.25	0.25	0.25
Q_{Air}		SCFM	1.9	1.9	1.9	1.9	1.9	1.9	1.9
$[C_{HNSO_5}]$	1	wt %	-	.009	.015	.015	0.19	.011	.015
	2	"	-	.038	.032	.032	.023	.037	.022
	3	"	-	.006	.002	.002	.015	.007	.007
$[C_{H_2SO_4}]$	1	wt %	-	78.7	79.1	79.1	78.6	79.1	78.2
	2	"	-	78.7	78.7	78.7	78.2	79.7	77.9
	3	"	-	78.6	78.9	78.9	78.9	79.4	78.3
$[C_{NO_2}]$	Flue Gas	ppm	540	550	620	600	330	530	850
	1	"	150	235	360	330	300	100✓	300
	2	"	-	350	320	350	-	-	370
	3	"	-	330	-	380	-	-	150
	4	"	-	-	-	-	-	-	-
$[C_{NO}]$	Flue Gas	ppm	825	700	450	475	150	400	1075
	1	"	350	275	150	150	150	300✓	475
	2	"	-	300	150	200	-	-	400
	3	"	-	2050	-	3025	-	-	2000
	4	"	-	-	-	-	-	-	-
NO_x Scrubbing Efficiency									
	10.0 ft.	%	-	-	-	-	-	-	-
	19.0 ft.		-	-	-	-	-	-	-
	26.5 ft.	"	63.5	59.3	52.3	55.4	-	57.2	60.0
NO_x Matl. Bal. Error		%	-	8.5	-2.3	-	-	-	43.0

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*Noisy run - levels hard to determine.
**New NO oxidizer - 0.05 ft^3.
✓Readings not steady.

Table IV-1. (Continued)

Run No.			79				80					
			A*	B	C	D	A	B	C	D	E	F
Relative Time		hr.	0	16.5	19.25	21.0	0	3.5	6.5	7.0	7.5	7.75
T_{NA}		°F	275/ 270	225/ 275	225/ 275	225/ 275	250/ 280	255/ 280	260/ 285	260/ 285	260/ 285	260/ 290
T_2 - Avg.		°F	262	259	259	259	269	265	267	267	267	267
T_4 - Avg.		°F	242	245	257	257	262	267	272	272	272	272
T_{HD}		°F	240/ 260	255/ 270	255/ 270	255/ 270	180/ 265	250/ 265	260/ 275	260/ 275	260/ 275	260/ 280
T_{HD} - Avg.		°F	252	260	260	260	227	259	267	267	267	267
Q Flue Gas		SCFM	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Q Acid		GPM	0.12	0.12	0.12	0.12	0.25	0.26	0.26	0.26	0.26	0.26
Q Air		SCFM	1.9	1.9	1.9	1.9	1.9	1.9	1.9	**	1.9	1.9
$[C_{HNSO_5}]$	1	wt %	.009	-	.015	.010	.022	.015	-	.015	-	-
	2	"	.018	-	.026	.040	.029	.019	-	.022	-	-
	3	"	.013	-	.007	.007	.022	.001	-	.011	-	-
$[C_{H_2SO_4}]$	1	wt %	78.7	-	80.2	79.6	80.0	79.8	-	80.7	-	-
	2	"	78.6	-	80.3	79.6	80.0	79.8	-	80.7	-	-
	3	"	78.6	-	80.0	79.6	80.0	79.8	-	80.7	-	-
$[C_{NO_2}]$	Flue Gas	ppm	500	470	490	840	570	460	490	515	-	550
	1	"	0	180	120	180	130	85	50	100	-	90
	2	"	190	-	-	-	-	-	-	185	-	190
	3	"	-	0	-	0	-	-	-	150	85	65
	4	"	-	-	-	-	-	-	-	-	-	-
$[C_{NO}]$	Flue Gas	ppm	450	450	450	825	550	500	500	425	-	425
	1	"	225	275	175	400	175	300	260	200	-	260
	2	"	150	-	-	-	-	-	-	110	-	125
	3	"	-	650	-	2500	-	-	-	1675	1100	1065
	4	"	-	-	-	-	-	-	-	-	-	-
NO_x Scrubbing Efficiency												
	10.0 ft.	%	-	-	-	-	-	-	-	-	-	-
	19.0 ft.	%	-	-	-	-	-	-	-	-	-	-
	26.5 ft.	%	70.0	50.5	69.0	67.5	67.0	60.0	68.7	68.2	-	62.1
NO_x Matl. Bal. Error		%	53.3	-	28.8	28.7	29.4	27.1	-	16.9	-	-

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*79A - Sample line problems: system cleaned.

**Probably about 30% lower than 1.9 .

Table IV-1. (Continued)

Run No.		81					82(a)						
		A	A'	B	C	D	A	B	C	D	E	F	G
Relative Time	hr.	0	0.25	1.5	2.5	4.0	0	2.0	4.75	5.5	6.0	6.75	7.5
T_{NA}	°F	260/ 280	260/ 280	255/ 285	255/ 285	255/ 285	220/ 280	245/ 280	260/ 295	265/ 295	265/ 295	270/ 275	270/ 295
T_2 - Avg.	°F	271	271	268	268	266	207	271	279	280	280	285	285
T_4 - Avg.	°F	271	271	272	272	274	235	269	271	271	271	273	273
T_{HD}	°F	260/ 280	260/ 280	265/ 280	265/ 280	265/ 280	245/ 270	250/ 270	265/ 290	280/ 300	280/ 300	285/ 305	285/ 305
T_{HD} - Avg.	°F	267	267	270	270	271	258	261	279	289	289	292	292
Q Flue Gas	SCFM	2.8	2.8	2.8	2.8	2.8	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Q Acid	GPM	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.23	0.23	0.23	0.23	0.23
Q Air	SCFM	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
$[C_{HNSO_5}]$ 1	wt %	.015	-	.008	.004	.003	.026	.017	-	.031	-	.035	-
2	"	.049	-	.013	.007	.014	.019	.026	-	.061	-	.068	-
3	"	.011	-	.011	.006	.006	.015	.011	-	.013	-	.010	-
$[C_{H_2SO_4}]$ 1	wt %	80.9	-	80.6	80.6	80.9	82.0	80.5	-	81.9	-	81.5	-
2	"	80.9	-	80.7	80.6	80.9	82.0	81.1	-	81.9	-	81.3	-
3	"	80.9	-	80.2	80.9	80.7	82.0	81.5	-	80.7	-	81.1	-
$[C_{NO_2}]$ Flue Gas	ppm	1100	-	1000	1000	1050	275	265	275	230	230	230	230
1	"	150	145	190	-	150	170	150	140	120	105	95	95
2	"	310	-	300	-	240	200	180	200	165	150	135	135
3	"	-	250	270	-	200	85	20	-	15	0	0	0
4	"	-	-	-	-	-	-	-	210	185	190	170	160
$[C_{NO}]$ Flue Gas	ppm	1080	-	1050	850	1050	250	235	450	275	235	235	235
1	"	325	260	260	-	250	170	100	250	225	140	155	250
2	"	160	-	125	-	160	175	100	225	150	135	135	135
3	"	-	2900	2150	-	2385	200	165	-	280	200	195	195
4	"	-	-	-	-	-	-	-	275	235	160	160	160
NO_x Scrubbing Efficiency													
10.0 ft.	%	-	-	-	-	-	-	-	33.2	7.8	24.7	29.0	31.2
19.0 ft.	%	-	-	-	-	-	28.5	44.0	41.4	37.7	38.7	41.9	41.9
26.5 ft.	"	78.3	81.5	78.0	-	81.0	34.3	50.0	45.0	31.8	47.4	47.3	47.3
NO_x Matl. Bal. Error	%	9.8	-	61.8	-	59.8	13.7	-10.9	-	-103	-	<-100	-

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

Table IV-1. (Continued)

Run No.		82(b)				82(c)		
		A	B	C	D	A	B	C*
Relative Time	hr.	0	0.75	2.0	3.0	0	1.5	3.5
T_{NA}	°F	265/ 300	275/ 300	265/ 295	270/ 300	270/ 300	270/ 300	270/ 300
T_2 - Avg.	°F	284	284	281	283	283	283	283
T_4 - Avg.	°F	271	284	279	277	277	277	277
T_{HD}	°F	285/ 310	285/ 310	280/ 300	280/ 305	265/ 305	265/ 305	265/ 305
T_{HD} - Avg.	°F	295	293	292	295	292	292	292
Q Flue Gas	SCFM	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Q Acid	GPM	0.23	0.23	0.23	0.23	0.24	0.24	0.24
Q Air	SCFM	1.9	1.9	1.9	1.9	1.9	1.9	3.8
$[C_{HNSO_5}]$ 1	wt %	-	-	.033	.037	.048	.041	.037
2	"	-	-	.059	.059	.066	.066	.066
3	"	-	-	.014	.011	.018	.022	.019
$[C_{H_2SO_4}]$ 1	wt %	-	-	80.6	80.7	81.3	81.3	81.5
2	"	-	-	80.9	80.7	81.5	81.3	81.5
3	"	-	-	81.1	81.1	81.3	81.1	81.3
$[C_{NO_2}]$ Flue Gas	ppm	485	-	490	490	1050	1050	1000
1	"	265	250	210	150	570	490	420
2	"	320	305	255	230	680	600	-
3	"	0	200	190	250	390	80	10
4	"	365	350	315	240	770	680	-
$[C_{NO}]$ Flue Gas	ppm	500	-	500	550	950	925	950
1	"	275	250	140	150	300	250	225
2	"	255	240	175	175	400	400	-
3	"	175	2600	2600	2900	4200	1550	1025
4	"	325	250	275	275	550	550	-
NO_x Scrubbing Efficiency		Not						
10.0 ft.	%	Steady	39.0	40.3	49.7	35.0	37.6	-
19.0 ft.	%	State	44.7	56.6	58.4	46.0	49.3	-
26.5 ft.	%	45.3	49.0	64.5	70.7	56.5	63.2	67.2
NO_x Matl.Bal.Error	%	-	-	~-50	-49.5	6.5	14.3	6.5
Stripper Matl.Bal.Error	%	-	-	-	-	-66.8	19.4	7.2

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*High stripper air.

Table IV-1. (Continued)

Run No.			83a	83b	83c	83a'	83b'	83c'		83b''	84a	
								A	B		A	B
Relative Time		hr.	-	-	-	-	-	0	1.0	-	0	1.5
T_{NA}		°F	275/ 310	255/ 295	260/ 285	250/ 275	260/ 290	280/ 285	280/ 295	260/ 280	275/ 285	275/ 280
T_2 - Avg.		°F	279	284	273	253	287	282	283	269	-	-
T_4 - Avg.		°F	295	265	272	265	275	280	287	269	280	279
T_{HD}		°F	240/ 270	235/ 270	230/ 270	250/ 275	260/ 275	270/ 280	270/ 290	270/ 285	265/ 285	270/ 285
T_{HD} - Avg.		°F	250	254	253	-	-	-	-	-	275	281
$Q_{Flue\ Gas}$		SCFM	8.6	8.6	8.6	8.8	8.8	8.8	8.8	8.8	6.0	6.0
Q_{Acid}		GPM	.40	.40	.40	.39	.38	.38	.39	.39	.40	.40
Q_{Air} (St)		SCFM	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	.6	.6
$[C_{HNSO_5}]$	1	wt %	.015	.018	.018	.022	.018	.029	.026	.018	.018	.015
	2	"	.022	.026	.037	.033	.029	.066	.070	.030	.025	.022
	3	"	.015	.018	.018	.014	.015	.018	.018	.015	.014	.011
$[C_{H_2SO_4}]$	1	wt %	80.9	80.7	80.9	80.9	80.8	80.4	80.9	82.6	79.4	79.4
	2	"	80.9	80.7	80.9	80.7	80.6	80.4	80.7	81.2	79.1	79.4
	3	"	80.9	80.7	80.9	80.9	81.3	80.6	82.3	82.0	79.1	79.4
$[C_{NO_2}]$ Flue Gas		ppm	320	480	1100	240	520	975	925	530	240	260
	1	"	0	0	0	65	320	490	455	250	60	80
	2	"	10	0	0	95	375	500	515	310	90	120
	3	"	50	10	5	15	130	340	300	100	50	0
	4	"	30	10	0	140	435	615	625	410	110	120
$[C_{NO}]$ Flue Gas		ppm	250	575	1000	240	475	1050	1000	490	300	275
	1	"	250	470	700	120	225	385	375	240	140	125
	2	"	300	475	700	125	275	500	460	275	160	125
	3	"	550	375	500	650	1000	2000	1975	1225	1675	1400
	4	"	325	475	650	150	350	635	575	360	240	175
NO_x Scrubbing Efficiency												
10.0 ft.		%	37.7	54.0	69.0	39.6	21.1	36.7	37.7	24.5	35.2	44.9
19.0 ft.		"	45.6	55.0	66.7	54.3	34.7	49.4	49.4	42.6	53.7	54.2
26.5 ft.		"	56.1	55.0	66.7	61.7	45.2	55.7	56.9	52.0	63.0	61.7
NO_x Matl. Bal. Error		%	21.6	31.1	42.6	6.7	16.2	12.7	7.8	20.2	-18.0	4.3

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

Table IV-1. (Continued)

Run No.		84b A	84b B	84c A	84c B	85c A	85c B*	85c C**	85c D**	85a A	85a B	85a C
Relative Time	hr.	0	1.0	0	0.5	0	5.0	5.25	6.0	0	1.25	1.75
T_{NA}	°F	280/ 280	275/ 275	270/ 280	260/ 280	265/ 290	-	-	-	270/ 315	245/ 310	245/ 310
T_2 - Avg.	°F	-	-	-	271	283	-	-	-	280	278	278
T_4 - Avg.	°F	280	274	274	270	276	-	-	-	292	278	278
T_{HD}		275/ 290	275/ 290	275/ 290	275/ 295	270/ 300	-	-	-	235/ 290	235/ 290	235/ 290
T_{HD} - Avg.	°F	281	281	281	285	289	-	-	-	269	269	269
$Q_{Flue\ Gas}$	SCFM	6.0	6.0	6.0	6.0	1.4	-	-	-	1.4	1.4	1.4
Q_{Acid}	GPM	.40	.40	.40	.40	0.1	-	-	-	.11	.13	.13
$Q_{Air\ (St)}$	SCFM	.6	.6	.6	.6	3.1	-	-	-	3.1	3.1	3.1
$[C_{HNSO_5}]$ 1	wt %	.015	.018	.019	.023	.019	-	-	-	-	.019	.022
2	"	.037	.037	.041	.038	.022	-	-	-	-	.022	.034
3	"	.011	.011	.008	.011	.011	-	-	-	-	.011	.015
$[C_{H_2SO_4}]$ 1	wt %	80.0	80.0	80.2	80.4	83.6	-	-	-	-	80.7	80.7
2	"	80.0	80.0	80.2	80.4	83.6	-	-	-	-	80.7	80.7
3	"	80.0	80.0	80.2	80.4	83.6	-	-	-	-	80.7	80.7
$[C_{NO_2}]$ Flue Gas	ppm	530	500	1050	1000	1000	950/ 1300	800/ 1300	840	200	210	230
1	"	190	200	415	420	60	35	40	10	0	5	30
2	"	270	-	515	-	95	-	-	15	0	25	-
3	"	280	-	1100	-	80	100	-	-	0	30	-
4	"	260	-	530	-	150	50	-	-	50	70	-
$[C_{NO}]$ Flue Gas	ppm	500	475	1050	1100	1250	950/ 875	1100/ 875	900	250	250	250
1	"	150	110	250	250	250	375	400	400	150	150	125
2	"	175	-	325	-	225	-	-	375	150	175	-
3	"	3025	-	6000	-	500	865	-	-	250	-	-
4	"	275	-	550	-	350	350	-	-	125	175	-
NO_x Scrubbing Efficiency												
10.0 ft.	%	48.1	-	48.7	-	77.7	-	-	-	-	46.7	-
19.0 ft.	%	56.1	-	60.0	-	85.8	-	-	-	-	56.5	-
26.5 ft.	"	67.0	68.2	68.3	68.1	86.2	78.5/ 81.3	79.5	-	-	66.3	67.7
NO_x Matl. Bal. Error	%	-1.8	-3.8	25.2	28.9	63.6	-	-	-	-	-14.7	-36.6

*Two measurements of feed level.

**Difficulty in achieving steady readings - sample lines probably plugged.

156

Table IV-1. (Continued)

Run No.			85b		85c		86a		86b		86b'			
			A	B	A	B*	A	B	A	B	A	B	C**	D
Relative Time		hr.	0	1.0	0	1.0	0	1.25	0	1.0	0	0.5	5.0	7.5
T_{NA}		°F	260/290	255/275	250/280	260/280	250/290	250/285	260/295	260/295	270/285	270/285	220/310	265/295
T_2 - Avg.		°F	276	260	263	270	269	272	279	281	278	278	268	281
T_4 - Avg.		°F	274	268	268	267	290	278	271	267	274	274	260	276
T_{HD}		°F	240/285	240/290	240/290	240/290	280/330	-	285/320	285/320	285/310	285/310	270/305	290/310
T_{HD} - Avg.		°F	265	267	268	267	312	-	306	299	296	296	285	303
Q Flue Gas		SCFM	1.4	1.4	1.4	1.4	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Q Acid		GPM	0.12	0.12	0.12	0.12	0.1	0.08	0.1	0.11	0.12	0.12	0.11	0.10
Q Air (St)		SCFM	3.1	3.1	3.1	3.1	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
[C_{HNSO_5}]	1	wt %	.023	.030	.041	-	.023	.018	.018	.024	.011	.011	.032	.013
	2	"	.038	.041	.114	-	.023	.026	.013	.009	.011	.013	.101	.090
	3	"	.011	.014	.023	-	.016	.0145	.015	.013	.013	.011	.052	.013
[$C_{H_2SO_4}$]	1	wt %	80.9	80.9	81.3	-	84.5	85.2	82.7	83.1	84.5	84.7	81.5	83.3
	2	"	80.9	80.9	81.3	-	84.5	83.3	81.3	83.1	82.7	83.1	82.3	80.5/
	3	"	80.9	80.9	81.3	-	84.3	84.0	81.9	84.5	83.6	84.5	82.2	82.5
[C_{NO_2}]	Flue Gas	ppm	550	540	1100	1100	230	250	550	570	510	510	540	525
	1	"	80	70	90	240	140	170	160	210	110	110	10	55
	2	"	140	110	130	-	150	190	-	25	140	155	90	95
	3	"	20	0	10	-	10	-	400	400	1140	1400	~1200	650
	4	"	210	150	180	-	130	1	-	305	200	125	-	110
[C_{NO}]	Flue Gas	ppm	475	500	1000	975	225	250	385	325	400	400	625	700
	1	"	100	100	75	100	90	100	~0	0	25	15	100	140
	2	"	125	125	90	-	100	100	-	10	85	100	135	150
	3	"	525	700	625	-	100	-	3900	3900	4050	3975	~5000	4400
	4	"	200	160	150	-	150	-	-	125	125	315	-	230
NO_x Scrubbing Efficiency														
	10.0 ft.	%	60.0	70.2	84.3	-	-	-	-	54.0	64.3	64.5	-	74.0
	19.0 ft.	"	74.1	77.4	89.5	-	45.5	42.0	-	70.5	-	72.0	80.5	79.9
	26.5 ft.	"	82.4	83.7	92.1	83.4	49.5	46.0	-	76.5	85.2	86.4	91.4	84.2
NO_x Matl. Bal. Error		%	-7.3	-5.0	-42.1	-	18.2	-13.2	68.7	<50	<50	68.5	13.2	-32.7

*Heater failed; copper powder exposed to acid in Scrubber 2.
**Acid flow variations - wide temperature fluctuations.
/System was cooled down between 5.0 and 7.5 hours and may have picked up some water.

Table IV-1. (Continued)

Run No.			86c		86d*	87a	87b	87c	88a	88b	88c	
											A	B
Relative Time		hr.	0	1.5	-	-	-	-	-	-	0	1.25
T_{NA}		°F	260/ 295	270/ 290	250/ 290	260/ 290	270/ 285	270/ 290	255/ 290	260/ 280	265/ 290	270/ 290
T_2 - Avg.		°F	283	284	270	273	278	275	284	273	280	278
T_4 - Avg.		°F	274	277	277	273	278	276	262	269	272	273
T_{HD}		°F	300/ 320	290/ 320	300/ 320	270/ 290	280/ 290	280/ 295	270/ 285	270/ 285	270/ 280	270/ 280
T_{HD} - Avg.		°F	305	306	312	279	285	287	274	275	274	272
Q Flue Gas		SCFM	2.9	2.9	2.9	4.9	4.9	4.9	2.9	2.9	2.9	2.9
Q Acid		GPM	0.1	0.1	0.1	.25	.25	.25	0.2	0.2	0.2	0.2
Q Air		SCFM	0.6	0.6	0.6	1.9	1.9	1.9	3.1	3.1	3.1	3.1
$[Q_{HNSO_5}]$	1	wt %	.026	.030	-	.015	.018	.029	.019	.027	.030	.034
	2	"	.106	.114	.329**	.022	.029	.081	.030	.038	.068	.061
	3	"	.015	.019	.038	.011	.015	.018	.011	.017	.022	.019
$[C_{H_2SO_4}]$	1	wt %	83.1	83.1	-	82.0	82.3	81.4	81.3	81.5	81.7	81.7
	2	"	82.5	83.1	82.3	81.6	81.9	81.2	81.3	81.5	81.7	81.7
	3	"	82.5	82.5	82.7	84.6	81.9	81.6	81.3	81.5	81.7	81.7
$[C_{NO_2}]$	Flue Gas	ppm	930	1000	1000	260	520	1000	230	510	1000	950
	1	"	15	15	-	120	205	365	70	130	150	130
	2	"	60	50	20	150	265	445	80	160	220	-
	3	"	790	780	490	90	430	1280	70	90	200	-
	4	"	110	100	60	185	350	580	90	230	340	-
$[C_{NO}]$	Flue Gas	ppm	1075	1050	1100	225	550	1000	280	490	950	1050
	1	"	125	125	-	110	150	180	160	150	350	350
	2	"	125	125	150	125	165	250	200	160	375	-
	3	"	4850	4700	-	475	2025	3390	250	640	1225	-
	4	"	225	175	175	140	300	390	340	225	475	-
NO_x Scrubbing Efficiency												
	10.0 ft.	%	83.3	86.6	88.9	33.0	39.3	51.5	33.3	54.5	58.2	-
	19.0 ft.	%	90.8	91.5	91.9	43.3	50.5	65.3	45.1	68.0	69.5	-
	26.5 ft.	"	93.0	93.6	-	52.6	67.5	72.8	54.9	72.0	74.4	76.0
NO_x Matl. Bal. Error		%	25.7	24.0	-79.0	4.1	35.8	5.9	-	-	-	-

*Run made with Scrubber 2 only (19-ft. of column). Fresh acid from stripper fed to Scrubber 2 directly.
**Concentration double-checked.

Table IV-1. (Continued)

Run No.		92a A*	92a B	92b A	92b B	92b C	92c A	92c B	93a A	93a B	93b A*	93b B
Relative Time	hr.	0	1.0	0	1.25	1.75						
T_{NA}	°F	260/295	265/300	255/280	260/290	-	250/285	-	260/290	-	260/305	-
T_2 - Avg.	°F	273	288	269	275	-	279	-	273	-	280	-
T_4 - Avg.	°F	280	270	270	273	-	269	-	271	-	271	-
T_{HD}	°F	270/295	285/300	290/300	280/300	-	285/295	-	280/290	-	280/300	-
T_{HD} - Avg.	°F	283	292	296	294	-	290	-	278	-	286	-
$Q_{Flue\ Gas}$	SCFM	4.9	4.9	4.9	4.9	-	4.9	-	2.6	-	2.6	-
Q_{Acid}	GPM	0.25	0.25	0.25	0.25	-	0.25	-	0.1	-	0.1	-
Q_{Air}	SCFM	0.9	0.9	0.9	0.9	-	0.9	-	1.6	-	1.6	-
$[C_{HNSO_5}]$ 1	wt %	.019	.019	-	0.02	-	.015	-	.011	-	.007	-
2	"	.026	.026	-	0.08	-	0.16	-	.049	-	.051	-
3	"	.008	.011	-	.007	-	.006	-	.009	-	.006	-
$[C_{H_2SO_4}]$ 1	wt %	81.5	81.5	-	82.1	-	80.9	-	82.1	-	81.8	-
2	"	81.5	81.5	-	81.9	-	80.8	-	80.8	-	81.3	-
3	"	81.5	81.5	-	81.9	-	80.9	-	81.2	-	81.1	-
$[C_{NO_2}]$ Flue Gas	ppm	270	270	480	560	450	1125	~1125	280	275	500	470
1	"	125	140	40	40	-	145	-	0	10	0	0
2	"	150	-	80	80	-	260	-	10	-	0	-
3	"	20	-	**	325	-	1100	-	0	-	0	-
4	"	160	-	160	130	-	420	-	25	-	10	-
$[C_{NO}]$ Flue Gas	ppm	250	240	550	470	575	1100	1150	225	225	475	500
1	"	125	125	160	150	-	120	-	85	100	150	150
2	"	140	-	175	160	-	175	-	100	-	135	-
3	"	1150	-	**	2375	-	4700	-	375	-	450	-
4	"	165	-	240	225	-	320	-	130	-	200	-
NO_x Scrubbing Efficiency 10.0 ft.	%	37.6	-	61.3	65.5	-	66.7	-	69.3	-	71.3	-
19.0 ft.	%	44.3	-	75.5	76.7	-	80.4	-	78.2	-	86.1	-
26.5 ft.	"	52.0	48.3	80.6	81.6	-	88.1	-	83.2	78.2	84.6	-
NO_x Matl. Bal. Error	%	-14.9	-7.8	-	-57.2	-	-50.8	-	-32.0	-	11.6	-

*All runs after 92 were made with 2 strippers in series.
**Pump broke - reading unsteady.

Table IV-1. (Continued)

Run No.			93c		94a		94b		94c		95a			
			A	B	A	B	A	B	A	B	A	B	C	D
Relative Time		hr.	0		0									
T_{NA}		°F	260/ 295	-	250/ 270	250/ 270	250/ 270	270/ 290	270/ 290	260/ 290	250/ 285	250/ 285	255/ 280	255/ 280
T_2 - Avg.		°F	274	-	264	264	264	273	273	268	258	258	271	271
T_4 - Avg.		°F	280	-	257	257	257	279	279	275	268	268	264	264
T_{HD}		°F	270/ 305	-	270/ 275	270/ 275	270/ 275	275/ 280	275/ 280	280/ 280	270/ 270	270/ 270	270/ 270	270/ 270
T_{HD} - Avg.		°F	286	-	272	272	273	279	279	279	272	272	272	272
$Q_{Flue\ Gas}$		SCFM	2.6	-	6.0	6.0	6.0	6.0	6.0	6.0	8.8	8.8	8.8	8.8
Q_{Acid}		GPM	0.1	-	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Q_{Air}		SCFM	1.6	-	1.6	1.6	1.6	1.6	1.6	1.6	0.3	0.3	0.3	0.3
$[Q_{HNSO_5}]$	1	wt %	.016	-	.023	.018	.026	.022	.030	.037	-	.019	-	-
	2	''	.096	-	.037	.030	.041	.034	.053	.056	-	.030	-	-
	3	''	.009	-	.011	.011	.015	.011	.015	.015	-	.011	-	-
$[C_{H_2SO_4}]$	1	wt %	81.1	-	81.3	81.3	81.3	81.3	81.3	81.3	-	80.7	-	-
	2	''	81.4	-	81.3	81.3	81.3	81.3	81.3	81.3	-	80.7	-	-
	3	''	80.4	-	81.3	81.3	81.3	81.3	81.3	81.3	-	80.7	-	-
$[C_{NO_2}]$	Flue Gas	ppm	1200	900	240	230	540	530	1100	1100	265	300	270	230
	1	''	10	0	50	30	90	80	300	290	100	135	-	85
	2	''	40	-	70	70	150	-	470	-	160	185	-	-
	3	''	-*	-	10	-	20	-	230	-	-	730	-	-
	4	''	190	-	130	120	280	-	630	-	-	220	-	-
$[C_{NO}]$	Flue Gas	ppm	1070	1025	225	241	550	525	1050	950	250	180	175	250
	1	''	200	175	200	225	250	280	350	375	180	135	-	175
	2	''	200	-	200	225	280	-	375	-	175	140	-	-
	3	''	-*	-	700	-	1100	-	1450	-	-	3250	-	-
	4	''	300	-	200	225	350	-	550	-	-	150	-	-
NO_x Scrubbing Efficiency														
	10.0 ft.	%	78.4	-	29.1	26.6	42.2	-	45.1	-	-	22.9	-	-
	19.0 ft.	%	89.4	-	40.8	37.2	60.6	-	60.7	-	35.0	32.3	-	-
	26.5 ft.	''	90.7	91.9	46.2	45.7	68.8	65.9	69.8	67.6	45.6	43.8	-	-
NO_x Matl. Bal. Error		%	29.3	-	-65.5	-39.3	2.4	4.9	23.4	10.0	-	-20.2	-	-

*Possible instrumentation problem - plugged sample lines.

Table IV-1. (Continued)

Run No.			95b		95c		
			A	B	A	B	C
Relative Time		hr.	0	0.75	0	1.75	3.25
T_{NA}		°F	255/280	250/280	245/280	260/285	260/285
T_2 - Avg.		°F	271	270	269	276	275
T_4 - Avg.		°F	264	263	264	267	277
T_{HD}		°F	270/270	275/280	270/290	280/280	260/285
T_{HD} - Avg.		°F	272	280	276	281	283
Q Flue Gas		SCFM	8.8	8.8	8.8	8.8	8.8
Q Acid		GPM	0.4	0.4	0.4	0.4	0.4
Q Air		SCFM	0.3	0.3	0.3	0.6	1.2
$[C_{HNSO_5}]$	1	wt %	.026	.023	.060	-	-
	2	"	.037	.033	.079	-	-
	3	"	.011	.015	.015	-	-
$[C_{H_2SO_4}]$	1	wt %	80.9	80.9	80.7	-	-
	2	"	80.9	80.9	80.7	-	-
	3	"	80.9	80.9	80.7	-	-
$[C_{NO_2}]$	Flue Gas	ppm	500	615	910	-	-
	1	"	190	320	310	-	-
	2	"	280	-	420	-	-
	3	"	2900	-	6500	5750	1700*
	4	"	360	-	570	-	-
$[C_{NO}]$	Flue Gas	ppm	550	575	950	-	-
	1	"	280	275	400	-	-
	2	"	300	-	475	-	-
	3	"	6000	-	8000	6000	4250*
	4	"	400	-	640	-	-
NO_x Scrubbing Efficiency							
	10.0 ft.	%	27.6	-	34.9	-	-
	19.0 ft.	"	44.8	-	51.9	-	-
	26.5 ft.	"	55.2	50.0	61.8	-	-
NO_x Matl. Bal. Error		%	7.8	17.0	-1.1	-	-

*Sharp drop - then slow decrease to these levels.

Table IV-1. (Continued)

Run No.			90a		90b		90c		90d	91a		91b	
			A	B	A	B	A	B		A	B	A	B
Relative Time		hr.	0	1.25	0	1.25	0	1.50	-	0	1.0	0	0.75
T_{NA}		°F	260/280	260/290	260/290	260/285	270/290	255/300	255/300	235/275	-	245/285	-
T_2 - Avg.		°F	271	275	275	277	278	283	283	261	-	262	-
T_4 - Avg.		°F	273	277	277	273	283	275	275	257	-	270	-
T_{HD}		°F	270/290	270/300	270/300	270/310	270/310	270/310	275/210	280/310	-	290/315	-
T_{HD} - Avg.		°F	281	281	281	287	288	289	289	297	-	298	-
$Q_{Flue\ Gas}$		SCFM	6.0	6.0	6.0	6.0	6.0	6.0	6.0	11.2	-	11.2	-
Q_{Acid}		GPM	.12	.12	.12	.12	.12	.12	.12	.1	-	.1	-
$Q_{Air\ (St)}$		SCFM	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	-	3.1	-
$[C_{HNSO_5}]$	1	wt %	.026	-	.034	-	.023	-	.037	.011	-	.019	-
	2	"	.037	-	.105	-	.265	-	.634	.022	-	.030	-
	3	"	.011	-	.015	-	.011	-	.019	.007	-	.011	-
$[C_{H_2SO_4}]$	1	wt %	80.4	-	80.7	-	81.3	-	81.3	81.7	-	82.3	-
	2	"	80.4	-	80.7	-	81.3	-	81.3	81.7	-	82.3	-
	3	"	80.4	-	80.7	-	81.3	-	81.3	81.7	-	82.3	-
$[C_{NO_2}]$	Flue Gas	ppm	270	[illegible]	490	470	1050	1100	2000	200	200	480	510
	1	"	130	100	250	220	450	450	900	140	160	240	250
	2	"	150	-	280	-	500	-	940	145	-	260	-
	3	"	0	-	10	-	50	-	130	400	-	80	-
	4	"	190	-	350	-	600	-	1100	160	-	300	-
$[C_{NO}]$	Flue Gas	ppm	250	275	550	525	1100	1100	2050	225	225	550	500
	1	"	125	150	225	175	275	290	375	175	175	350	300
	2	"	150	-	240	-	350	-	475	200	-	460	-
	3	"	260	-	640	-	1775	-	2600	60	-	1100	-
	4	"	175	-	260	-	500	-	700	225	-	450	-
NO_x Scrubbing Efficiency													
	10.0 ft.	%	29.8	-	41.3	-	48.8	-	55.5	9.4	-	27.2	-
	19.0 ft.	%	42.4	-	50.0	-	60.5	-	65.1	18.8	-	35.9	-
	26.5 ft.	"	51.0	52.5	54.3	60.5	66.3	66.4	68.5	25.8	21.2	42.7	45.5
NO_x Matl. Bal. Error		%	8.8	-	-14.4	-	-30.7	-	-53.5	13.4	-	34.7	-

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

Table IV-1. (Continued)

Run No.		91c		91d		96a		96b		96c	
		A	B	A	B	A	B	A	B	A	B
Relative Time	hr.	0	1.50	0		0	1.0	0	1.75	0	1.0
T_{NA}	°F	250/ 295	-	250/ 305	-	270/ 280	265/ 290	240/ 285	240/ 290	265/ 290	-
T_2 - Avg.	°F	262	-	263	-	277	275	275	274	272	-
T_4 - Avg.	°F	278	-	278	-	275	276	267	269	278	-
T_{HD}	°F	295/ 310	-	290/ 305	-	280/ 295	380/ 310	280/ 320	240/ 310	295/ 305	-
T_{HD} - Avg.	°F	303	-	300	-	288	291	302	302	302	-
$Q_{Flue\ Gas}$	SCFM	11.2	-	11.2	-	1.5	1.5	1.5	1.5	1.5	-
Q_{Acid}	GPM	.1	-	.1	-	.12	.12	.13	.13	.13	-
$Q_{Air\ (St)}$	SCFM	3.1	-	3.1	-	.3	.3	.3	.3	.3	-
$[C_{HNSO_5}]$ 1	wt %	.034	-	.046	-	.007	-	.006	-	.011	-
2	"	.205	-	.589	-	.018	-	.048	-	.075	-
3	"	.015	-	.023	-	.007	-	.008	-	.007	-
$[C_{H_2SO_4}]$ 1	wt %	82.7	-	82.9	-	80.1	-	81.0	-	80.2	-
2	"	82.7	-	82.9	-	80.3	-	80.2	-	80.2	-
3	"	82.7	-	82.9	-	80.3	-	80.4	-	80.6	-
$[C_{NO_2}]$ Flue Gas	ppm	1100	1150	2000	2000	240	260	520	500	900	1000
1	"	400	475	280	300	0	10	35	0	10	10*
2	"	490	-	420	-	50	-	20*	-	90	-
3	"	170	-	660	-	0	-	565	-	490	-
4	"	660	-	710	-	120	-	380*	-	210	-
$[C_{NO}]$ Flue Gas	ppm	1050	1075	2100	2050	290	300	550	550	1000	1000
1	"	450	480	650	550	150	125	175	300*	200	175*
2	"	525	-	750	-	110	-	225*	-	225	-
3	"	2400	-	4100	-	1000	-	2375	-	3250	-
4	"	650	-	1000	-	140	-	225*	-	350	-
NO_x Scrubbing Efficiency 10.0 ft.	%	39.1	-	58.3	-	50.9	-	43.5	-	70.5	-
19.0 ft.	"	52.8	-	71.5	-	69.8	-	77.1	-	83.7	-
26.5 ft.	"	60.5	57.1	77.3	79.0	71.7	75.9	80.4	73.2	88.9	90.8
NO_x Mat'l Bal. Error	%	27.2	-	25.9	-						

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*Erratic response - probably UV cell contamination.

Table IV-1. (Continued)

Run No.			97a		97b		97c		98a		98b	
			A	B	A	B	A	B	A	B	A	B
Relative Time		hr.	0	1.25	0	1.25	0	1.0	0	1.0	0	1.25
T_{NA}		°F	240/280	250/280	250/290	250/280	250/285	250/285	250/280	245/280	240/275	240/275
T_2 - Avg.		°F	258	261	263	265	268	268	264	261	260	260
T_4 - Avg.		°F	259	269	270	263	268	272	267	263	271	271
T_{HD}		°F	270/280	270/285	275/280	270/285	280/290	280/290	280/290	280/290	280/290	280/290
T_{HD} - Avg.		°F	274	279	279	279	285	287	288	287	285	285
$Q_{Flue\ Gas}$		SCFM	4.9	4.9	4.9	4.9	4.9	4.9	8.6	8.6	8.6	8.6
Q_{Acid}		GPM	.25	.25	.25	.25	.25	.25	.25	.25	.25	.25
$Q_{Air\ (St)}$		SCFM	.9	.9	.9	.9	.9	.9	.9	.9	.9	.9
$[C_{HNSO_5}]$	1	wt %	.019	-	.006	-	.005	-	.007	-	.007	-
	2	"	.023	-	.047	-	.094	-	.031	-	.046	-
	3	"	.011	-	.006	-	.007	-	.009	-	.006	-
$[C_{H_2SO_4}]$	1	wt %	80.4	-	80.3	-	80.2	-	80.4	-	79.8	-
	2	"	80.4	-	80.2	-	79.9	-	80.0	-	79.5	-
	3	"	80.4	-	80.3	-	80.0	-	80.0	-	79.8	-
$[C_{NO_2}]$	Flue Gas	ppm	280	270	500	480	1025	1000	265	270	475	480
	1	"	175	170	155	170	360	360	160	155	240	245
	2	"	195	-	225	-	500	-	200	-	305	-
	3	"	50	-	160	-	560	-	30	-	165	-
	4	"	220	-	295	-	590	-	230	-	355	-
$[C_{NO}]$	Flue Gas	ppm	225	225	500	550	1090	1125	265	275	525	550
	1	"	100	100	220	180	220	235	170	200	285	285
	2	"	100	-	250	-	285	-	175	-	300	-
	3	"	950	-	1950	-	4600	-	1650	-	1410	-
	4	"	125	-	350	-	500	-	225	-	375	-
NO_x Scrubbing Efficiency												
	10.0 ft.	%	31.7	-	35.5	-	48.5	-	14.2	-	27.0	-
	19.0 ft.	%	41.6	-	52.5	-	62.9	-	29.2	-	39.5	-
	26.5 ft.	"	45.5	45.5	62.5	66.0	72.6	72.0	32.7	34.9	47.5	48.5

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

Table IV-1. (Continued)

Run No.		99a A	99a B	99a C	99b A	99b B	99c	99d A	99d B	100a	100b
Relative Time	hr.	0	0.50	1.50	0	0.75	-	0	1.00	-	-
T_{NA}	°F	-	-	185/ 210	190/ 210	-	190/ 210	190/ 215	-	180/ 210	185/ 210
T_2 - Avg.	°F	-	-	193	199	-	200	199	-	199	195
T_4 - Avg.	°F	-	-	197	198	-	201	201	-	185	199
T_{HD}	°F	-	-	275/ 380	270/ 280	-	275/ 280	275/ 280	-	250/ 260	200/ 230
T_{HD} - Avg.	°F	-	-	278	277	-	279	278	-	255	223
$Q_{Flue\ Gas}$	SCFM	-	-	4.9	4.9	-	4.9	4.9	-	4.9	4.9
Q_{Acid}	GPM	-	-	.25	.25	-	.25	.25	-	.62	.62
$Q_{Air\ (St)}$	SCFM	-	-	.9	.9	-	.9	.9	-	.9	.9
$[C_{HNSO_5}]$ 1	wt %	-	-	.009	.009	-	.017	.021	-	.006	.006
2	"	-	-	.020	.043	-	.100	.197	-	.027	.056
3	"	-	-	.008	.007	-	.009	.011	-	.006	.004
$[C_{H_2SO_4}]$ 1	wt %	-	-	72.9	73.0	-	73.0	73.1	-	74.7	74.4
2	"	-	-	72.5	72.6	-	72.7	72.8	-	74.0	74.0
3	"	-	-	72.5	73.0	-	72.9	73.0	-	74.2	74.2
$[C_{NO_2}]$ Flue Gas	ppm	280	385	255	530	520	1050*	2050	2050	270	535*
1	"	180	215	110	200	205	360	670	670	10	40
2	"	230	-	130	260	-	460	830	-	15	110
3	"	45	-	65	135	-	515	1550	-	280	1000
4	"	270	-	175	335	-	575	955	-	-	-
$[C_{NO}]$ Flue Gas	ppm	275	250	300	555	560	1060*	2025	2100	270	555*
1	"	125	125	175	245	260	225	300	300	125	300
2	"	125	-	180	255	-	275	400	-	135	300
3	"	1300	-	1125	1550	-	4290	~5800	-	2325	3225
4	"	170	-	250	350	-	475	750	-	-	-
NO_x Scrubbing Efficiency											
10.0 ft.	%	20.7	-	23.4	36.9	-	50.2	58.2	-	-	-
19.0 ft.	%	36.0	-	44.1	52.5	-	65.2	69.8	-	72.2	67.4
26.5 ft.	"	45.0	46.5	48.6	59.0	56.9	72.3	76.2	76.6	75.0	68.8

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*Erratic response - probably UV cell contamination.

Table IV-1. (Continued)

Run No.			100c			101b		101c		101d		102a	
			A	B	C	A	B	A	B	A	B	A	B
Relative Time		hr.	0			0		0		0		0	
T_{NA}		°F	185/ 210	-	-	-	-	240/ 300	-	240/ 290	-	210/ 290	-
T_2 - Avg.		°F	192	-	-	-	-	283	-	281	-	276	-
T_4 - Avg.		°F	192	-	-	-	-	270	-	257	-	251	-
T_{HD}		°F	220/ 230	-	-	-	-	260/ 265	-	260/ 270	-	265/ 275	-
T_{HD} - Avg.		°F	226	-	-	-	-	262	-	265	-	269	-
$Q_{Flue\ Gas}$		SCFM	4.9	-	-	4.9	-	4.9	-	4.9	-	4.9	-
Q_{Acid}		GPM	.62	-	-	.25	-	.25	-	.25	-	.25	-
$Q_{Air\ (St)}$		SCFM	.9	-	-	.9	-	.9	-	.9	-	.9	-
$[C_{HNSO_5}]$	1	wt %	.010	-	-	.015	-	.018	-	.018	-	.018	-
	2	"	.093	-	-	.022	-	.022	-	.022	-	.026	-
	3	"	.006	-	-	.011	-	.015	-	.011	-	.011	-
$[C_{H_2SO_4}]$	1	wt %	74.3	-	-	79.1	-	79.1	-	79.1	-	79.1	-
	2	"	73.6	-	-	79.1	-	79.1	-	79.1	-	79.1	-
	3	"	74.3	-	-	79.1	-	79.1	-	79.1	-	79.1	-
$[C_{NO_2}]$	Flue Gas	ppm	1100	1050	1100	120	65	240	220	320	330	350	350
	1	"	195	-	-	30	20	40	-	40	-	240	250
	2	"	295	275	-	30	-	60	-	60	-	260	-
	3	"	210	-	-	30	-	120	-	370	-	75	-
	4	"	-	-	-	60	-	95	-	110	-	270	-
$[C_{NO}]$	Flue Gas	ppm	1025	1060	975	650	650	1150	1150	2200	2325	75	75
	1	"	160	-	-	500	460	850	-	1675	-	60	40
	2	"	175	225	-	475	-	850	-	1700	-	60	-
	3	"	4350	-	-	900	-	1725	-	3025	-	175	-
	4	"	-	-	-	475	-	875	-	1800	-	60	-
NO_x Scrubbing Efficiency													
	10.0 ft.	%	-	-	-	30.5	-	30.2	-	24.2	-	22.4	-
	19.0 ft.	"	78.0	76.3	-	34.4	-	34.5	-	30.2	-	24.7	-
	26.5 ft.	"	83.3	-	-	31.2	32.9	36.0	-	31.9	-	29.4	29.4

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

Table IV-1. (Continued)

Run No.			102b		102c	102d
Relative Time		hr.	0		-	-
T_{NA}		°F	210/ 290	-	220/ 285	230/ 295
T_2 - Avg.		°F	275	-	277	278
T_4 - Avg.		°F	247	-	251	260
T_{HD}		°F	270/ 275	-	270/ 270	265/ 270
T_{HD} - Avg.		°F	271	-	270	268
$Q_{Flue\ Gas}$		SCFM	4.9	-	4.9	4.9
Q_{Acid}		GPM	.25	-	.25	.25
$Q_{Air\ (St)}$		SCFM	.9	-	.9	.9
$[C_{HNSO_5}]$	1	wt %	.018	-	.022	.026
	2	"	.033	-	.041	.059
	3	"	.015	-	.018	.018
$[C_{H_2SO_4}]$	1	wt %	79.1	-	79.1	79.1
	2	"	79.1	-	79.1	79.1
	3	"	79.1	-	79.1	79.1
$[C_{NO_2}]$	Flue Gas	ppm	490	500	1000*	2000
	1	"	330	330	620	1300
	2	"	360	-	700	1350
	3	"	110	-	220	490
	4	"	380	-	705	1350
$[C_{NO}]$	Flue Gas	ppm	100	100	225*	350
	1	"	60	60	100	175
	2	"	75	-	110	200
	3	"	500	-	725	925
	4	"	75	-	130	225
NO_x Scrubbing Efficiency						
	10.0 ft.	%	22.9	-	31.8	33.0
	19.0 ft.	%	26.3	-	33.9	34.0
	26.5 ft.	"	33.9	35.0	41.2	37.2

Key to Effluent Streams: 1 - NO_x scrubber 4 (7.5 ft.); 2 - NO_x scrubber 2 (19 ft.)
3 - stripper; 4 - NO_x scrubber 2 (halfway up the 19 ft. scrubber).

*Erratic response - probably UV cell contamination.

APPENDIX V. METAL ION INTERFERENCE IN SCRUBBER AND STRIPPER OPERATION

A. $HNSO_5$ Determination — Interference by Corrosion Products

During the course of miniplant experimentation it was necessary to analyze the acid streams for $HNSO_5$ content. The standard procedure, whereby acid samples are titrated to a pale pink endpoint with aqueous 0.1N $KMnO_4$ solution, was found to indicate inordinately high concentrations of oxidizable material in the acid streams. Calculations of available material and our past experience with similar experiments led us to believe that oxidizable materials other than $HNSO_5$ must be present in the acid. The source of these interfering materials was believed to be corrosion products of metal alloys exposed to the acid streams. Visible spectrophotometric analysis, laboratory corrosion tests, and replacement of some of the parts of the miniplant equipment suggested that the major source of corrosion products was probably stainless steel. Of the possible stainless steel locations in the acid feed stream, the strippers offered the highest surface area if the Teflon lining had failed. Dismantling and inspection of the interior of the strippers revealed that the Teflon lining had failed and severe corrosion had occurred.

The principle components of SS316 are iron, chromium, nickel, manganese, and molybdenum. If the reaction of any of these species with carbon is rapid or if corrosion is rapid, then one or more of them could be in a reduced state while present in the acid. Titration with permanganate would then result in an indication of oxidizable material present which could be mistaken for $HNSO_5$. Iron in sulfuric acid could be present as Fe^{+2} or Fe^{+3}; chromium as Cr^{+2} or Cr^{+3} (oxidation to chromate is slow and occurs only with very strong oxidants; nickel as Ni^{+2}; manganese as Mn^{+2}, Mn^{+3}, Mn^{+4} (oxidation to permanganate would be unlikely; and molybdenum as Mo^{+2}, Mo^{+3}, Mo^{+4}, Mo^{+5}, and perhaps Mo^{+6}. Contact with the air for a sufficient period of time would probably be sufficient to oxidize any of them somewhat. We have found that samples which give high errors by $KMnO_4$ titration (relative to nitrometer results) when recently removed from the miniplant give much smaller errors by $KMnO_4$ titration after a week's storage in a closed container. A small error, equivalent to perhaps 0.04 wt % $HNSO_5$, is still observed (relative to the nitrometer results). Experiments with synthetically prepared solutions using chromic and nitrosylsulfuric acid solutions lead us to believe that this error is due to the slow oxidation of chromic ion to chromate by $KMnO_4$. Nitrosylsulfuric acid does not oxidize chromic ion to chromate.

Interference by corrosion products can be avoided by using the nitrometer to analyze for $HNSO_5$ instead of the $KMnO_4$ titration. Other titrimetric methods can probably be developed; however, the time required for such an undertaking would be excessive, considering the availability of the nitrometer procedure.

B. Effect of the Presence of Corrosion Products on $HNSO_5$ Solubility and Scrubber Performance

The presence of corrosion products could lessen scrubber performance by decreasing the solubility of $HNSO_5$ at any given partial pressures of NO and NO_2. This effect would be observed on the scrubber column as a decrease in overall scrubbing efficiency. However, all sections of a large scrubber would have the same efficiency per unit length. Thus, if the bottom section of the scrubber was scrubbing NO_x from the gas phase, the top section would further reduce the gas phase NO_x concentration as long as the acid entering the column was free of dissolved $HNSO_5$.

One may treat the problem of decreased $HNSO_5$ solubility in the following semiquantitative manner. The dissolution reaction is:

$$NO + NO_2 + 2H_2SO_4 = 2NO^+ + 2HSO_4^- + H_2O \ .$$

One may write an equilibrium constant expression for this reaction:

$$K = \frac{[NO^+]^2[HSO_4^-]^2[H_2O]}{p_{NO}p_{NO_2}[H_2SO_4]^2} \ .$$

If one sets $p_{NO} = p_{NO_2} = p$ and if one disregards small changes in solvent concentrations (i.e., H_2O and H_2SO_4), this expression reduces to:

$$K = \frac{[NO^+]^2[HSO_4^-]^2}{p^2} \ ,$$

and it may be rearranged to solve for $HNSO_5$ solubility:

$$HNSO_5 = [NO^+] = \frac{P\sqrt{K}}{[HSO_4^-]} \ .$$

$HNSO_5$, which dissociates in sulfuric acid to form NO^+ and HSO_4^-, decreases in solubility as the HSO_4^- concentration increases. If any increase occurs in HSO_4^- concentration, the solubility of $HNSO_5$ decreases proportionately.

We know that corrosion products are present in the hot scrubber acid at a concentration close to the saturation value. Precipitation of metal salts is observed during cooling of the system. We can estimate the concentration of dissolved metal salts to be several moles per liter from a casual observation of the volume of solids which precipitate out when scrubber acid samples are cooled. The solids content is approximately 5 vol %. The corrosion products are undoubtedly present as bisulfates, since there are no other anions present in appreciable concentration. Since the metal ions which we would expect to be present are polyvalent, there will be at least two bisulfate ions present for each metal ion which is present. We may conservatively estimate that the increase in bisulfate ion due to the presence of corrosion products in the scrubber is 5 M.

Now that we have estimated the increase in bisulfate concentration, we must estimate the original bisulfate concentration if we are to obtain a proper notion of the expected decrease in $HNSO_5$ solubility. Ionization Constants of Acids and Bases, by Albert and Serjeant, lists for the first dissociation of H_2SO_4 a pK_a of −3.0. The Hammet acidity function is −3.0 at a sulfuric acid concentration of 6 M, according to the same authors. Using these two values and simple mass balance expressions for H_2O, H_3O^+, HSO_4^-, and H_2SO_4, one may estimate that at 80 wt % H_2SO_4 (14 M H_2SO_4), the bisulfate concentration is approximately 4 M at room temperature. At the higher temperatures encountered in the scrubber, the extent of dissociation is probably greater and the bisulfate concentration might be 5 or 6 M.

Thus, the concentration of bisulfate is approximately 5 M in the absence of corrosion products and might be as high as 10 M in the presence of corrosion products. This doubling of bisulfate concentration would result in halving of the $HNSO_5$ solubility according to the equations we developed above. This decrease in solubility could halve the efficiency of the scrubber. Thus, the scrubbing efficiency, which is about 70%, might well be expected to provide higher recoveries of NO_x in the absence of excessive amounts of corrosion products.

The number of assumptions involved in our treatment of $HNSO_5$ solubility (and its dependence on corrosion products) makes it advisable that we consider the results of our calculations to be semiquantitative. It would be possible to measure $HNSO_5$ solubility in the presence and absence of corrosion products.

C. Effect of the Presence of Corrosion Products on Stripper Performance

The performance of the stripper directly affects the extent to which the scrubber may remove NO_x from the gas phase. If the feed acid to the scrubber contains residual $HNSO_5$ that was not removed by the stripper, then there will be a residual gas phase NO_x level equal to or greater than the equilibrium partial pressure of NO_x corresponding to the equilibrium value for the feed acid. The behavior of the scrubber will be such that the lower portions of the scrubber will operate fairly well (because of the high gas phase NO_x input levels), but the upper sections of the scrubber will remove very little more NO_x (due to the residual liquid phase $HNSO_5$).

Corrosion products present in the acid loop precipitate out of solution when the system is cooled. This problem is probably very serious in the stripper, where precipitation can result in the blockage of pores in the activated charcoal and a resultant drastic decrease in available surface area. Such blocking could drastically reduce stripper performance. This is a difficult hypothesis to check directly, but the scrubber behavior supports this view.

APPENDIX VI. CORROSION IN MINIPLANT EQUIPMENT

A. Pumps

At the beginning of the testing we employed three Eco gear pumps made of Hastelloy B bodies with carbon wear plates and bearings. This construction was recommended for the application by the manufacturer, whose experience indicated that these materials would withstand the corrosive nature of hot sulfuric acid and, in fact, claimed that other similar pumps were sold for this purpose. Examination of standard corrosion tables indicated that the Hastelloy B material was marginal for long-term application, but should be satisfactory for a period of several months.

One pump was purchased early in the program, tested under the desired operating conditions, and showed the capability of pumping over one gallon per minute of hot sulfuric acid (only 0.4 GPM was required for the test series). Upon this successful evaluation, two more identical pumps were purchased and installed in the system.

When the testing was begun, it was noticed that the pump capacity seemed to drop somewhat as the temperature increased. Extended operation of the system caused all three pumps to eventually lose their capability to pump the minimum required quantity of acid. The pumps failed in order of their installation into the system. Examination of the interior of the pumps showed that there was extensive corrosion and erosion of the pump bodies as well as the drive shaft and the drive gears. The pump manufacturer was shown the results of only a few days of operation, and he recommended replacement of the Hastelloy B drive gear with a carbon drive gear, but this did not prove to be adequate. The corrosion of the pump bodies created a large clearance between the pumping gears and the bodies, and the resulting back slip of fluid prevented adequate pumping.

The pump manufacturer cooperated with us to the extent that he supplied us with samples of his pump parts to evaluate in the desired application, but it is clear that the highly corrosive conditions aggravated by the highly turbulent conditions present in a gear pump plus the presence of air bubbles causing aeration of the corrosive fluid all combine to rule out the use of available materials in our system. As shown in Fig. VI-1, samples of Hastelloy B, Hastelloy C, Carpenter 20, and stainless steel 316L all failed quite badly under the plant's operating conditions. (Note: An obvious question would be how our Carpenter 20 piston pumps have survived almost 2 yr of intermittant use without apparent failure. The answer appears to be in the na-

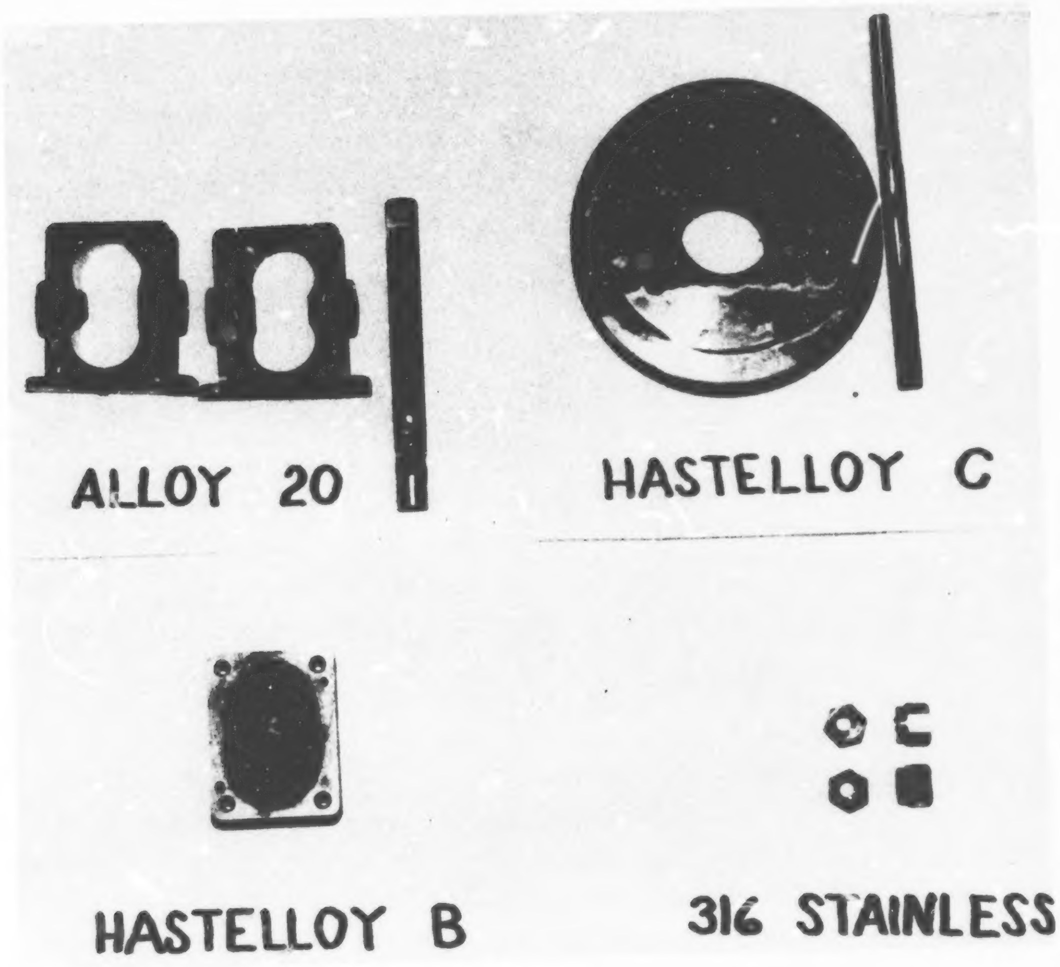
ALLOY 20
HASTELLOY C
HASTELLOY B
316 STAINLESS

Fig. VI-1. Photographs of corroded pump parts showing comparison with untreated parts; the Hastelloy B sample came from one of the Eco pumps in miniplant service.

ture of the piston pump, which is essentially a low-speed mechanism with no tight tolerance requirements. Both the piston and the pump head cavity could corrode slowly under the non-turbulent conditions of this pump's operation and there would be little or no danger of pump failure. The only problem might involve the ball checks and, indeed, these did show signs of excessive corrosion and reduced operating efficiency.)

This experience with the pumps did provide a qualitative input to the program in terms of the utility of various materials of construction. Clearly, Hastelloy B and C are incapable of standing up to the corrosive nature of the liquid system. Carpenter 20 is marginal and may be of value in certain applications.

B. Strippers

As mentioned in Appendix II, examination of the strippers after 2 to 3 weeks of operation showed that the Teflon coating had undergone catastrophic failure. When the cover of one of the strippers was removed, the appearance of the coating was as shown in Fig. VI-2. The acid had obviously penetrated the Teflon at a great many points, apparently through pinholes in the coating. The acid then corroded the stainless steel of the stripper walls and the coating was peeled back as the corrosion occurred in a circular manner. The result was that the coating failure took the form of a great many small circles being cut out of the Teflon. Many of these circles interconnected with each other and some of the coating came off in lace-like films. In other areas the coating was completely removed, and there was a thick (up to 1/4 in.) buildup of precipitated metal salts on the walls. It should be noted that the coating used was recommended by duPont for this application, with the actual coating applied by a duPont approved vendor.

A light-colored precipitate was obtained by cooling the acid circulated through the system. X-ray diffraction analysis of this precipitate disclosed that the material was $Fe_2(SO_4)_3$.

This experience indicates that Teflon coating is virtually worthless in this type of application. It is also apparent that Type 316L stainless steel is unusable for hot nitrosylsulfuric acid solutions. It should be pointed out that Teflon lining of equipment has not been ruled out by this work and remains to be tested. (Teflon lining has the advantage of being a relatively thick, continuous layer applied by extrusion techniques as opposed to the thin spray-and-bake application of the Teflon coating which is prone to pinholes.)

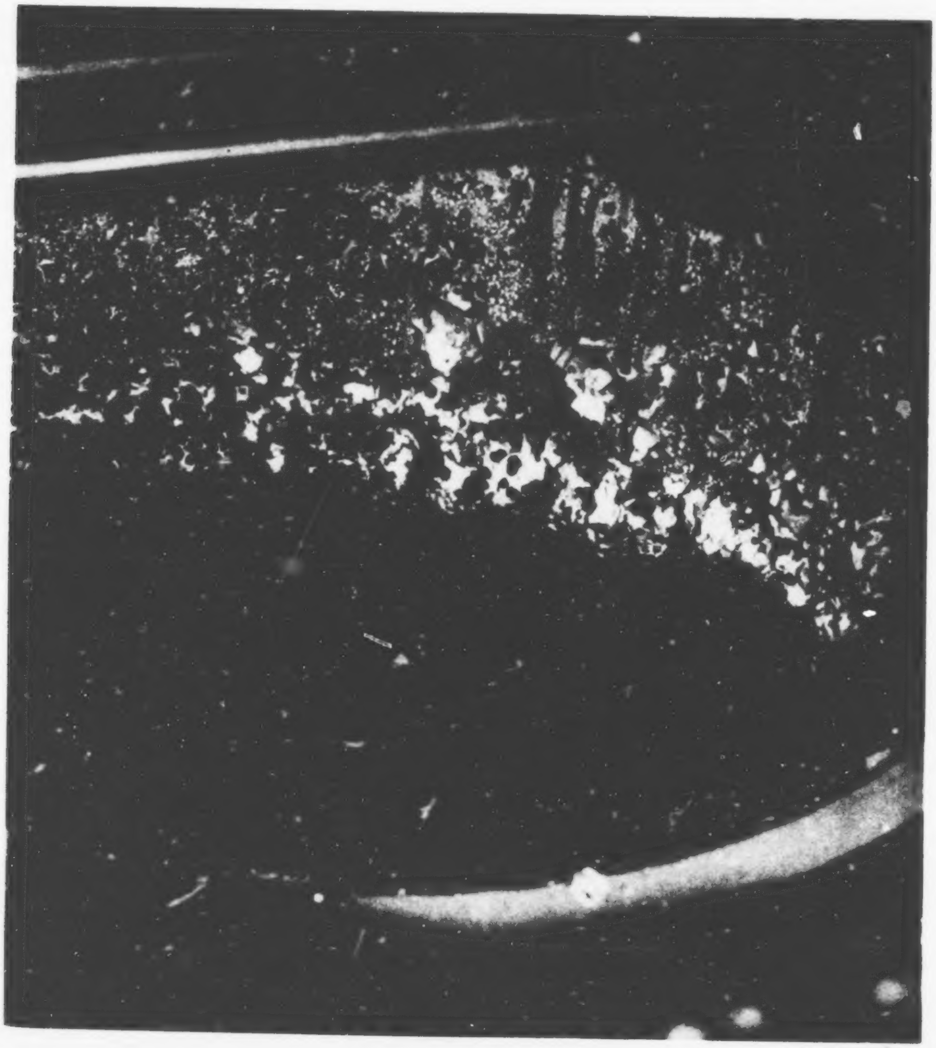

Fig. VI-2. Photograph of the top of a stripper column after 3 weeks service showing damaged coating.

APPENDIX VII. MATHEMATICAL ANALYSIS OF SCRUBBER/STRIPPER DATA

Table VII-1. Tyco Scrubbing Data Summary Sheet

Table VII-2. Average Values of NO_x Error

Table VII.3. Tyco Scrubbing Data

Table VII-4. OAP Scrubbing Data

Table VII-5. Computer Program for Tyco Data

Table VII-6. Computer Program for OAP Data

Table VII-7. Rate Constants from the Tyco Data

Table VII-8. Rate Constants from the OAP Data

Table VII-1. Tyco Scrubbing Data Summary Sheet

RUN	Q	NO INLET	NO 27 FT	NO2 INLET	NO2 27 FT	DNO	DNO2	NOX ERROR
82AB	4.9	235	100	265	150	135	115	20
82BD	4.9	550	150	470	150	400	320	80
82CB	4.9	925	250	1050	490	675	560	115
83AP	8.8	240	120	240	65	120	175	-55
83BP	8.8	475	225	520	320	250	200	50
83CPB	8.8	1000	375	925	455	625	470	155
84AB	6.0	275	125	260	80	150	180	-30
84BA	6.0	500	150	530	190	350	340	10
84CA	6.0	1050	250	1050	415	800	635	165
85AB	1.4	250	150	210	5	100	205	-105
85BB	1.4	500	100	540	70	400	470	-70
85CPA	1.4	1000	75	1100	90	925	1010	-85
86AA	2.9	225	90	230	140	135	90	45
86BPD	2.9	700	140	525	55	560	470	90
86CB	2.9	1050	125	1000	15	925	985	-60
87A	4.9	225	110	260	120	115	140	-25
87B	4.9	550	150	520	205	400	315	85
87C	4.9	1000	180	1000	365	820	635	185
92AA	4.9	250	125	270	125	125	145	-20
92BB	4.9	470	150	560	40	320	520	-200
92CA	4.9	1100	120	1125	145	980	980	0
93AA	2.6	225	85	280	0	140	280	-140
93BA	2.6	475	150	500	0	325	500	-175
93CA	2.6	1070	200	1200	10	870	1190	-320
94AB	6.0	240	225	230	30	15	200	-185
94BA	6.0	550	250	540	90	300	450	-150
94CA	6.0	1050	350	1100	300	700	800	-100
95AB	8.8	180	135	300	135	45	165	-120
95BA	8.8	550	280	500	190	270	310	-40
95CA	8.8	950	400	910	310	550	600	-50
96AA	1.5	290	150	240	0	140	240	-100
96BA	1.5	550	175	520	35	375	485	-110
96CA	1.5	1000	200	900	10	800	890	-90
97AA	4.9	225	100	280	175	125	105	20
97BA	4.9	500	220	500	155	280	345	-65
97CA	4.9	1090	220	1025	360	870	665	205

Table VII-2. Average Values of NO_x Error (at 95% Confidence Level)

For 80's NO_x error = 32 ± 180

For 90's NO_x error = -91 ± 220

For 80's + 90's NO_x error = -30 ± 230

For 250 ppm NO_x error = -58 ± 140

For 500 ppm NO_x error = -41 ± 200

For 1000 ppm NO_x error = 10 ± 300

Table VII-3. Tyco Scrubbing Data

		NO				NO2			
RUN	Q	INLET	9.5FT	19 FT	27 FT	INLET	9.5FT	19 FT	27 FT
82AB	4.9	235	200	100	100	265	200	180	150
82BD	4.9	550	275	175	150	470	240	230	150
82CB	4.9	925	550	400	250	1050	680	600	490
83AP	8.8	240	150	125	120	240	140	95	65
83BP	8.8	475	350	275	225	520	435	375	320
83CPB	8.8	1000	575	460	375	925	625	515	455
84AB	6.0	275	175	125	125	260	120	120	80
84BA	6.0	500	275	175	150	530	260	270	190
84CA	6.0	1050	550	325	250	1050	530	515	415
85AB	1.4	250	175	175	150	210	70	25	5
85BB	1.4	500	160	125	100	540	150	110	70
85CPA	1.4	1000	150	90	75	1100	180	130	90
86AA	2.9	225	150	100	90	230	130	150	140
86BPD	2.9	700	230	150	140	525	110	95	55
86CB	2.9	1050	175	125	125	1000	100	50	15
87A	4.9	225	140	125	110	260	185	150	120
87B	4.9	550	300	165	150	520	350	265	205
87C	4.9	1000	390	250	180	1000	580	445	365
92AA	4.9	250	165	140	125	270	160	150	125
92BB	4.9	470	225	160	150	560	130	80	40
92CA	4.9	1100	320	175	120	1125	420	260	145
93AA	2.6	225	130	100	85	280	25	10	0
93BA	2.6	475	200	135	150	500	0	0	0
93CA	2.6	1070	300	200	200	1200	190	40	10
94AB	6.0	240	225	225	225	230	120	70	30
94BA	6.0	550	350	280	250	540	280	150	90
94CA	6.0	1050	550	375	350	1100	630	470	300
95AB	8.8	180	150	140	135	300	220	185	135
95BA	8.8	550	400	300	280	500	360	280	190
95CA	8.8	950	640	475	400	910	570	420	310
96AA	1.5	290	140	110	150	240	120	50	0
96BA	1.5	550	225	225	175	520	380	20	35
96CA	1.5	1000	350	225	200	900	210	90	10
97AA	4.9	225	125	100	100	280	220	195	175
97BA	4.9	500	350	250	220	500	295	225	155
97CA	4.9	1090	500	285	220	1025	590	500	360

178

Table VII-4. OAP Scrubbing Data[10]

	NO		NO2				
RUN	INLET	OUTLET	INLET	OUTLET	DNO	DNO2	NOX ERROR
14-1	273	215	260	209	58	51	7
14-2	370	268	355	263	102	92	10
14-3	475	330	450	319	145	131	14
14-4	575	368	550	352	207	198	8
14-5	695	434	661	419	261	242	19
14-6	813	553	793	415	259	378	-119
15-1	256	204	256	206	52	49	2
15-2	343	258	351	260	85	91	-6
15-3	451	331	452	324	120	128	-8
15-4	555	393	556	385	162	171	-9
15-5	664	463	664	453	200	211	-11
15-6	769	521	800	529	248	270	-23
17-1	253	187	253	167	66	86	-20
17-2	366	266	348	230	101	119	-18
17-3	462	331	436	276	131	160	-29
17-4	598	405	562	340	193	222	-29
17-5	681	446	664	402	235	262	-27
17-6	758	486	770	457	273	313	-40
18-1	253	199	249	207	55	42	13
18-2	345	260	340	250	85	91	-6
18-3	450	335	445	338	115	107	7
18-4	552	400	553	391	152	162	-9
18-5	651	448	652	456	203	196	7
18-6	769	522	786	529	247	257	-10

Table VII-5. Computer Program for Tyco Data

```
/RATES/
11.02 !SJM/ CALCULATION OF RATE CONSTANTS FOR C-141 SCRUBBING EXPERIMENTS
ON NO AND NO2
11.03 A=PI/36.0, CJ=0
11.04 H1=26.5,H2=19.0,H4=9.5
11.05 DEMAND INP,OUP
11.06 OPEN INP FOR INPUT AS FILE 3
11.07 OPEN OUP FOR OUTPUT AS FILE 4
11.08 TYPE "
  RUN   GAS  HEIGHT   AHG-1      P0/PX      LN(P0/PX)  1/P0-1/PX     K1         K2
  ---   ---  ------   -----      -----      ---------  ---------     --         --

"
11.21 READ FROM 3: X,Q,N20,N21,N22,N24,N10,N11,N12,N14
11.211 DO PART 13
11.22 DO PART 12
11.225 CJ=CJ+1
11.226 DO PART 14 IF FP CJ/5=0 !PAGING ROUTINE
11.23 TO STEP 11.21
12.21 R11=(N10/N11),R12=(N10/N12),R14=(N10/N14)
12.22 L11=LOG(R11),L12=LOG(R12),L14=LOG(R14)
12.23 AG1=(A*H1)/Q,AG2=(A*H2)/Q,AG4=(A*H4)/Q
12.24 F11=L11/AG1,F12=L12/AG2,F14=L14/AG4
12.311 R21=(N20/N21),R22=(N20/N22),R24=(N20/N24)
12.312 L21=LOG(R21),L22=LOG(R22),L24=LOG(R24)
12.313 F21=L21/AG1,F22=L22/AG2,F24=L24/AG4
12.321 D11=(1/N10)-(1/N11),D12=(1/N10)-(1/N12),D14=(1/N10)-(1/N14)
12.322 S11=-D11/AG1,S12=-D12/AG2,S14=-D14/AG4
12.331 D21=(1/N20)-(1/N21),D22=(1/N20)-(1/N22),D24=(1/N20)-(1/N24)
12.332 S21=-D21/AG1,S22=-D22/AG2,S24=-D24/AG4
12.401 TYPE IN FORM 69: X,H1,AG1,R11,L11,D11,F11,S11
12.4011 WRITE ON 4 IN FORM 69: X,H1,AG1,R11,L11,D11,F11,S11
12.402 TYPE IN FORM 69: X,H2,AG2,R12,L12,D12,F12,S12
12.4021 WRITE ON 4 IN FORM 69: X,H2,AG2,R12,L12,D12,F12,S12
12.403 TYPE IN FORM 69: X,H4,AG4,R14,L14,D14,F14,S14
12.4031 WRITE ON 4 IN FORM 69: X,H4,AG4,R14,L14,D14,F14,S14
12.404 TYPE " "
12.411 TYPE IN FORM 70: X,H1,AG1,R21,L21,D21,F21,S21
12.4111 WRITE ON 4 IN FORM 70: X,H1,AG1,R21,L21,D21,F21,S21
12.412 TYPE IN FORM 70: X,H2,AG2,R22,L22,D22,F22,S22
12.4121 WRITE ON 4 IN FORM 70: X,H2,AG2,R22,L22,D22,F22,S22
12.413 TYPE IN FORM 70: X,H4,AG4,R24,L24,D24,F24,S24
12.4131 WRITE ON 4 IN FORM 70: X,H4,AG4,R24,L24,D24,F24,S24
12.414 TYPE "

"
13.11 !SHORT PART TO IGNORE ANY INCOMPLETE DATA SET
13.12 CM=0.000001
13.21 TO STEP 11.21 IF Q=CM
13.22 TO STEP 11.21 IF N20=CM
13.23 TO STEP 11.21 IF N21=CM
13.24 TO STEP 11.21 IF N22=CM
13.25 TO STEP 11.21 IF N24=CM
13.26 TO STEP 11.21 IF N10=CM
13.27 TO STEP 11.21 IF N11=CM
13.28 TO STEP 11.21 IF N12=CM
13.29 TO STEP 11.21 IF N14=CM
14.11 TYPE "&L

"
14.12 DO STEP 11.08
```

Table VII-6. Computer Program for OAP Data[10]

```
/GRATES/
11.02 !SJM/ CALCULATION OF RATE CONSTANTS FOR C-141 SCRUBBING EXPERIMENTS
ON NO AND NO2
11.03 A=(PI/4)*(2.25/12)*(2.25/12), CJ=0
11.04 H1=1.5
11.05 DEMAND OUP
11.06 OPEN /LGD2/ FOR INPUT AS FILE 3
11.07 OPEN OUP FOR OUTPUT AS FILE 4
11.08 TYPE "
  RUN   GAS  HEIGHT   AHG-1       P0/PX      LN(P0/PX)  1/P0-1/PX      K1          K2
  ---   ---  ------   -----       -----      ---------  ---------      --          --
"
11.21 READ FROM 3: X,N20,N21,N10,N11
11.22 DO PART 12
11.225 CJ=CJ+1
11.226 DO PART 14 IF FP CJ/30=0 !PAGING ROUTINE
11.23 TO STEP 11.21
12.21 R11=(N10/N11)
12.22 L11=LOG(R11)
12.23 AG1=(A*H1)/Q
12.24 F11=L11/AG1
12.311 R21=(N20/N21)
12.312 L21=LOG(R21)
12.313 F21=L21/AG1
12.321 D11=(1/N10)-(1/N11)
12.322 S11=-D11/AG1
12.331 D21=(1/N20)-(1/N21)
12.332 S21=-D21/AG1
12.401 TYPE IN FORM 69: X,H1,AG1,R11,L11,D11,F11,S11
12.4011 WRITE ON 4 IN FORM 69: X,H1,AG1,R11,L11,D11,F11,S11
12.411 TYPE IN FORM 70: X,H1,AG1,R21,L21,D21,F21,S21
12.4111 WRITE ON 4 IN FORM 70: X,H1,AG1,R21,L21,D21,F21,S21
14.11 TYPE "&L

"
14.12 DO STEP 11.08
15.11 !SJM-DRC, CONVERSION OF LOU GARCIA GRAPHICAL DATA, FEB 1972
15.12 Q=20/60, NCT=24, CNT=0
15.21 OPEN /LGD/ FOR INPUT AS FILE 5
15.22 OPEN /LGD2/ FOR OUTPUT AS FILE 6
15.31 READ FROM 5: X,X1C, Y1C, X2C, Y2C
15.32 CNT=CNT+1
15.41 N10=100*10^(0.0752*X1C)
15.42 R1A=(2.5E-5)*10^(0.07265*Y1C)
15.43 N11=N10-((R1A*(9.91E6)/60)/Q)
15.46 N20=100*10^(0.07525*X2C)
15.47 R2A=(2.5E-5)*10^(0.07265*Y2C)
15.48 N21=N20-((R2A*(9.91E6)/60)/Q)
15.51 WRITE ON 6 IN FORM 6: X, N20, N21, N10, N11
15.61 TO STEP 15.81 IF CNT=NCT
15.62 TO STEP 15.31
15.81 CLOSE 5
15.82 CLOSE 6
15.83 DO PART 11

FORM 6:
'%%%%%%',#############,#############,#############,####.#########
```

Table VII-7. Rate Constants from the Tyco Data

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
82AB	"NO"	26.50	4.720E-01	2.350E+00	8.544E-01	-5.745E-03	1.810E+00	1.217E-02
82AB	"NO"	19.00	3.384E-01	2.350E+00	8.544E-01	-5.745E-03	2.525E+00	1.698E-02
82AB	"NO"	9.50	1.692E-01	1.175E+00	1.613E-01	-7.447E-04	9.532E-01	4.401E-03
82AB	"NO2"	26.50	4.720E-01	1.767E+00	5.691E-01	-2.893E-03	1.206E+00	6.120E-03
82AB	"NO2"	19.00	3.384E-01	1.472E+00	3.868E-01	-1.782E-03	1.143E+00	5.266E-03
82AB	"NO2"	9.50	1.692E-01	1.325E+00	2.814E-01	-1.226E-03	1.663E+00	7.249E-03
82BD	"NO"	26.50	4.720E-01	3.667E+00	1.299E+00	-4.848E-03	2.753E+00	1.027E-02
82BD	"NO"	19.00	3.384E-01	3.143E+00	1.145E+00	-3.896E-03	3.384E+00	1.151E-02
82BD	"NO"	9.50	1.692E-01	2.000E+00	6.931E-01	-1.818E-03	4.097E+00	1.075E-02
82BD	"NO2"	26.50	4.720E-01	3.133E+00	1.142E+00	-4.539E-03	2.420E+00	9.618E-03
82BD	"NO2"	19.00	3.384E-01	2.043E+00	7.147E-01	-2.220E-03	2.112E+00	6.561E-03
82BD	"NO2"	9.50	1.692E-01	1.958E+00	6.721E-01	-2.039E-03	3.972E+00	1.205E-02
82CB	"NO"	26.50	4.720E-01	3.700E+00	1.308E+00	-2.919E-03	2.772E+00	6.185E-03
82CB	"NO"	19.00	3.384E-01	2.312E+00	8.383E-01	-1.419E-03	2.477E+00	4.193E-03
82CB	"NO"	9.50	1.692E-01	1.682E+00	5.199E-01	-7.371E-04	3.073E+00	4.357E-03
82CB	"NO2"	26.50	4.720E-01	2.143E+00	7.621E-01	-1.088E-03	1.615E+00	2.306E-03
82CB	"NO2"	19.00	3.384E-01	1.750E+00	5.596E-01	-7.143E-04	1.654E+00	2.111E-03
82CB	"NO2"	9.50	1.692E-01	1.544E+00	4.345E-01	-5.182E-04	2.568E+00	3.063E-03
83AP	"NO"	26.50	2.628E-01	2.000E+00	6.931E-01	-4.167E-03	2.638E+00	1.596E-02
83AP	"NO"	19.00	1.884E-01	1.920E+00	6.523E-01	-3.833E-03	3.462E+00	2.036E-02
83AP	"NO"	9.50	9.421E-02	1.600E+00	4.700E-01	-2.500E-03	4.989E+00	2.654E-02
83AP	"NO2"	26.50	2.692E-01	3.692E+00	1.306E+00	-1.122E-02	4.971E+00	4.269E-02
83AP	"NO2"	19.00	1.884E-01	2.526E+00	9.268E-01	-6.360E-03	4.919E+00	3.375E-02
83AP	"NO2"	9.50	9.421E-02	1.714E+00	5.390E-01	-2.976E-03	5.721E+00	3.159E-02
83BP	"NO"	26.50	2.628E-01	2.111E+00	7.472E-01	-2.339E-03	2.843E+00	8.901E-03
83BP	"NO"	19.00	1.884E-01	1.727E+00	5.465E-01	-1.531E-03	2.901E+00	8.126E-03
83BP	"NO"	9.50	9.421E-02	1.357E+00	3.054E-01	-7.519E-04	3.242E+00	7.981E-03
83BP	"NO2"	26.50	2.628E-01	1.625E+00	4.855E-01	-1.202E-03	1.848E+00	5.574E-03
83BP	"NO2"	19.00	1.884E-01	1.387E+00	3.269E-01	-7.436E-04	1.735E+00	3.947E-03
83BP	"NO2"	9.50	9.421E-02	1.195E+00	1.785E-01	-3.758E-04	1.895E+00	3.989E-03

Table VII-7. (Cont.)

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
83CPB	"NO"	26.50	2.628E-01	2.667E+00	9.808E-01	-1.667E-03	3.732E+00	6.342E-03
83CPB	"NO"	19.00	1.884E-01	2.174E+00	7.765E-01	-1.174E-03	4.121E+00	6.230E-03
83CPB	"NO"	9.50	9.421E-02	1.739E+00	5.534E-01	-7.391E-04	5.874E+00	7.846E-03
83CPB	"NO2"	26.50	2.628E-01	2.033E+00	7.095E-01	-1.117E-03	2.790E+00	4.249E-03
83CPB	"NO2"	19.00	1.884E-01	1.796E+00	5.856E-01	-8.607E-04	3.108E+00	4.568E-03
83CPB	"NO2"	9.50	9.421E-02	1.480E+00	3.920E-01	-5.189E-04	4.161E+00	5.508E-03
84AB	"NO"	26.50	3.854E-01	2.200E+00	7.885E-01	-4.364E-03	2.046E+00	1.132E-02
84AB	"NO"	19.00	2.763E-01	2.200E+00	7.885E-01	-4.364E-03	2.853E+00	1.579E-02
84AB	"NO"	9.50	1.382E-01	1.571E+00	4.520E-01	-2.078E-03	3.271E+00	1.504E-02
84AB	"NO2"	26.50	3.854E-01	3.250E+00	1.179E+00	-8.654E-03	3.058E+00	2.245E-02
84AB	"NO2"	19.00	2.763E-01	2.167E-00	7.732E-01	-4.487E-03	2.798E+00	1.624E-02
84AB	"NO2"	9.50	1.382E-01	2.167E+00	7.732E-01	-4.487E-03	5.596E+00	3.248E-02
84BA	"NO"	26.50	3.854E-01	3.333E+00	1.204E+00	-4.667E-03	3.124E+00	1.211E-02
84BA	"NO"	19.00	2.763E-01	2.857E+00	1.050E+00	-3.714E-03	3.799E+00	1.344E-02
84BA	"NO"	9.50	1.382E-01	1.818E-00	5.978E-01	-1.636E-03	4.327E+00	1.184E-02
84BA	"NO2"	26.50	3.854E-01	2.789E+00	1.026E+00	-3.376E-03	2.662E+00	8.760E-03
84BA	"NO2"	19.00	2.763E-01	1.963E+00	6.745E-01	-1.817E-03	2.441E+00	6.575E-03
84BA	"NO2"	9.50	1.382E-01	2.038E+00	7.122E-01	-1.959E-03	5.154E+00	1.418E-02
84CA	"NO"	26.50	3.854E-01	4.200E+00	1.435E+00	-3.048E-03	3.723E+00	7.907E-03
84CA	"NO"	19.00	2.763E-01	3.231E+00	1.173E+00	-2.125E-03	4.244E+00	7.688E-03
84CA	"NO"	9.50	1.382E-01	1.909E+00	6.466E-01	-8.658E-04	4.680E+00	6.266E-03
84CA	"NO2"	26.50	3.854E-01	2.530E+00	9.283E-01	-1.457E-03	2.408E+00	3.781E-03
84CA	"NO2"	19.00	2.763E-01	2.039E+00	7.124E-01	-9.894E-04	2.578E+00	3.580E-03
84CA	"NO2"	9.50	1.382E-01	1.981E+00	6.837E-01	-9.344E-04	4.948E+00	6.763E-03
85AB	"NO"	26.50	1.652E+00	1.667E+00	5.108E-01	-2.667E-03	3.092E-01	1.614E-03
85AB	"NO"	19.00	1.184E+00	1.429E+00	3.567E-01	-1.714E-03	3.012E-01	1.447E-03
85AB	"NO"	9.50	5.922E-01	1.429E+00	3.567E-01	-1.714E-03	6.023E-01	2.895E-03
85AB	"NO2"	26.50	1.652E+00	4.200E+01	3.738E+00	-1.952E-01	2.263E+00	1.162E-01
85AB	"NO2"	19.00	1.184E+00	8.400E+00	2.128E+00	-3.524E-02	1.797E+00	2.975E-02
85AB	"NO2"	9.50	5.922E-01	3.000E+00	1.099E+00	-9.524E-03	1.855E+00	1.608E-02

183

Table VII-7. (Cont.)

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
85BB	"NO"	26.50	1.652E+00	5.000E+00	1.609E+00	-8.000E-03	9.743E-01	4.843E-03
85BB	"NO"	19.00	1.184E+00	4.000E+00	1.386E+00	-6.000E-03	1.171E+00	5.066E-03
85BB	"NO"	9.50	5.922E-01	3.125E+00	1.139E+00	-4.250E-03	1.924E+00	7.177E-03
85BB	"NO2"	26.50	1.652E+00	7.714E+00	2.0-.3E+00	-1.243E-02	1.237E+00	7.527E-03
85BB	"NO2"	19.00	1.184E+00	4.909E+00	1.591E+00	-7.239E-03	1.343E+00	6.112E-03
85BB	"NO2"	9.50	5.922E-01	3.600E+00	1.281E+00	-4.815E-03	2.163E+00	8.131E-03
85CPA	"NO"	26.50	1.652E+00	1.333E+01	2.590E+00	-1.233E-02	1.568E+00	7.466E-03
85CPA	"NO"	19.00	1.184E+00	1.111E+01	2.408E+00	-1.011E-02	2.033E+00	8.537E-03
85CPA	"NO"	9.50	5.922E-01	6.667E+00	1.897E+00	-5.667E-03	3.204E+00	9.569E-03
85CPA	"NO2"	26.50	1.652E+00	1.222E+01	2.503E+00	-1.020E-02	1.515E+00	6.176E-03
85CPA	"NO2"	19.00	1.184E+00	8.462E+00	2.136E+00	-6.783E-03	1.803E+00	5.727E-03
85CPA	"NO2"	9.50	5.922E-01	6.111E+00	1.810E+00	-4.646E-03	3.057E+00	7.847E-03
86AA	"NO"	26.50	7.974E-01	2.500E+00	9.163E-01	-6.667E-03	1.149E+00	8.360E-03
86AA	"NO"	19.00	5.717E-01	2.250E+00	8.109E-01	-5.556E-03	1.418E+00	9.717E-03
86AA	"NO"	9.50	2.859E-01	1.500E+00	4.055E-01	-2.222E-03	1.418E+00	7.773E-03
86AA	"NO2"	26.50	7.974E-01	1.643E+00	4.964E-01	-2.795E-03	6.225E-01	3.505E-03
86AA	"NO2"	19.00	5.717E-01	1.533E+00	4.274E-01	-2.319E-03	7.476E-01	4.056E-03
86AA	"NO2"	9.50	2.859E-01	1.769E+00	5.705E-01	-3.344E-03	1.996E+00	1.170E-02
86BPD	"NO"	26.50	7.974E-01	5.000E+00	1.609E+00	-5.714E-03	2.018E+00	7.166E-03
86BPD	"NO"	19.00	5.717E-01	4.667E+00	1.540E+00	-5.238E-03	2.694E+00	9.162E-03
86BPD	"NO"	9.50	2.859E-01	3.043E+00	1.113E+00	-2.919E-03	3.893E+00	1.021E-02
86BPD	"NO2"	26.50	7.974E-01	9.545E+00	2.256E+00	-1.628E-02	2.829E+00	2.041E-02
86BPD	"NO2"	19.00	5.717E-01	5.526E+00	1.710E+00	-8.622E-03	2.990E+00	1.508E-02
86BPD	"NO2"	9.50	2.859E-01	4.773E+00	1.563E+00	-7.186E-03	5.467E+00	2.514E-02
86CB	"NO"	26.50	7.974E-01	8.400E+00	2.128E+00	-7.048E-03	2.669E+00	8.838E-03
86CB	"NO"	19.00	5.717E-01	8.400E+00	2.128E+00	-7.048E-03	3.722E+00	1.333E-02
86CB	"NO"	9.50	2.859E-01	6.000E+00	1.792E+00	-4.762E-03	6.268E+00	1.666E-02
86CB	"NO2"	26.50	7.974E-01	6.667E+01	4.200E+00	-6.567E-02	5.267E+00	8.235E-02
86CB	"NO2"	19.00	5.717E-01	2.000E+01	2.996E+00	-1.900E-02	5.240E+00	3.323E-02
86CB	"NO2"	9.50	2.859E-01	1.000E+01	2.303E+00	-9.000E-03	8.055E+00	3.148E-02

Table VII-7. (Cont.)

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
87A	"NO"	26.50	4.720E-01	2.045E+00	7.156E-01	-4.646E-03	1.516E+00	9.845E-03
87A	"NO"	19.00	3.384E-01	1.800E+00	5.878E-01	-3.556E-03	1.737E+00	1.051E-02
87A	"NO"	9.50	1.692E-01	1.607E+00	4.745E-01	-2.696E-03	2.804E+00	1.595E-02
87A	"NO2"	26.50	4.720E-01	2.167E+00	7.732E-01	-4.487E-03	1.638E+00	9.508E-03
87A	"NO2"	19.00	3.384E-01	1.733E+00	5.500E-01	-2.821E-03	1.626E+00	8.335E-03
87A	"NO2"	9.50	1.692E-01	1.405E+00	3.403E-01	-1.559E-03	2.011E+00	9.216E-03
87B	"NO"	26.50	4.720E-01	3.667E+00	1.299E+00	-4.848E-03	2.753E+00	1.027E-02
87B	"NO"	19.00	3.384E-01	3.333E+00	1.204E+00	-4.242E-03	3.558E+00	1.254E-02
87B	"NO"	9.50	1.692E-01	1.833E+00	6.061E-01	-1.515E-03	3.583E+00	8.955E-03
87B	"NO2"	26.50	4.720E-01	2.537E+00	9.308E-01	-2.955E-03	1.972E+00	6.261E-03
87B	"NO2"	19.00	3.384E-01	1.962E+00	6.741E-01	-1.851E-03	1.992E+00	5.469E-03
87B	"NO2"	9.50	1.692E-01	1.486E+00	3.959E-01	-9.341E-04	2.340E+00	5.521E-03
87C	"NO"	26.50	4.720E-01	5.556E+00	1.715E+00	-4.556E-03	3.633E+00	9.653E-03
87C	"NO"	19.00	3.384E-01	4.000E+00	1.386E+00	-3.000E-03	4.097E+00	8.866E-03
87C	"NO"	9.50	1.692E-01	2.564E+00	9.416E-01	-1.564E-03	5.565E+00	9.245E-03
87C	"NO2"	26.50	4.720E-01	2.740E+00	1.008E+00	-1.740E-03	2.136E+00	3.686E-03
87C	"NO2"	19.00	3.384E-01	2.247E+00	8.097E-01	-1.247E-03	2.239E+00	3.686E-03
87C	"NO2"	9.50	1.692E-01	1.724E+00	5.447E-01	-7.241E-04	3.220E+00	4.280E-03
92AA	"NO"	26.50	4.720E-01	2.000E+00	6.931E-01	-4.000E-03	1.469E+00	8.475E-03
92AA	"NO"	19.00	3.384E-01	1.786E+00	5.798E-01	-3.143E-03	1.714E+00	9.288E-03
92AA	"NO"	9.50	1.692E-01	1.515E+00	4.155E-01	-2.061E-03	2.456E+00	1.218E-02
92AA	"NO2"	26.50	4.720E-01	2.160E+00	7.701E-01	-4.296E-03	1.632E+00	9.103E-03
92AA	"NO2"	19.00	3.384E-01	1.800E+00	5.878E-01	-2.963E-03	1.737E+00	8.756E-03
92AA	"NO2"	9.50	1.692E-01	1.687E+00	5.232E-01	-2.546E-03	3.093E+00	1.505E-02
92BB	"NO"	26.50	4.720E-01	3.133E+00	1.142E+00	-4.539E-03	2.420E+00	9.618E-03
92BB	"NO"	19.00	3.384E-01	2.937E+00	1.078E+00	-4.122E-03	3.184E+00	1.218E-02
92 BB	"NO"	9.50	1.692E-01	2.089E+00	7.366E-01	-2.317E-03	4.354E+00	1.369E-02
92BB	"NO2"	26.50	4.720E-01	1.400E+01	2.639E+00	-2.321E-02	5.502E+00	4.919E-02
92BB	"NO2"	19.00	3.384E-01	7.000E+00	1.946E+00	-1.071E-02	5.751E+00	3.166E-02
92BB	"NO2"	9.50	1.692E-01	4.308E+00	1.460E+00	-5.907E-03	8.632E+00	3.491E-02

Table VII-7. (Cont.)

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
92CA	"NO"	26.50	4.720E-01	9.167E+00	2.216E+00	-7.424E-03	4.694E+00	1.573E-02
92CA	"NO"	19.00	3.384E-01	6.286E+00	1.838E+00	-4.805E-03	5.433E+00	1.420E-02
92CA	"NO"	9.50	1.692E-01	3.437E+00	1.235E+00	-2.216E-03	7.296E+00	1.310E-02
92CA	"NO2"	26.50	4.720E-01	7.759E+00	2.049E+00	-6.008E-03	4.341E+00	1.273E-02
92CA	"NO2"	19.00	3.384E-01	4.327E+00	1.465E+00	-2.957E-03	4.329E+00	8.739E-03
92CA	"NO2"	9.50	1.692E-01	2.679E+00	9.853E-01	-1.492E-03	5.824E+00	8.819E-03
93AA	"NO"	26.50	8.894E-01	2.647E+00	9.734E-01	-7.320E-03	1.094E+00	8.230E-03
93AA	"NO"	19.00	6.377E-01	2.250E+00	8.109E-01	-5.556E-03	1.272E+00	8.712E-03
93AA	"NO"	9.50	3.189E-01	1.731E+00	5.486E-01	-3.248E-03	1.720E+00	1.019E-02
93AA	"NO2"	26.50	8.894E-01	2.800E+07	1.715E+01	-1.000E+05	1.928E+01	1.124E+06
93AA	"NO2"	19.00	6.377E-01	2.800E+01	3.332E+00	-9.643E-02	5.225E+00	1.512E-01
93AA	"NO2"	9.50	3.189E-01	1.120E+01	2.416E+00	-3.643E-02	7.577E+00	1.142E-01
93BA	"NO"	26.50	8.894E-01	3.167E+00	1.153E+00	-4.561E-03	1.296E+00	5.128E-03
93BA	"NO"	19.00	6.377E-01	3.519E+00	1.258E+00	-5.302E-03	1.973E+00	8.314E-03
93BA	"NO"	9.50	3.189E-01	2.375E+00	8.650E-01	-2.895E-03	2.713E+00	9.078E-03
93BA	"NO2"	26.50	8.894E-01	5.000E+07	1.773E+01	-1.000E+05	1.993E+01	1.124E+06
93BA	"NO2"	19.00	6.377E-01	5.000E+07	1.773E+01	-1.000E+05	2.780E+01	1.568E+05
93BA	"NO2"	9.50	3.189E-01	5.000E+07	1.773E+01	-1.000E+05	5.560E+01	3.136E+05
93CA	"NO"	26.50	8.894E-01	5.350E+00	1.677E+00	-4.065E-03	1.886E+00	4.571E-03
93CA	"NO"	19.00	6.377E-01	5.350E+00	1.677E+00	-4.065E-03	2.630E+00	6.375E-03
93CA	"NO"	9.50	3.189E-01	3.567E+00	1.272E+00	-2.399E-03	3.988E+00	7.523E-03
93CA	"NO2"	26.50	8.894E-01	1.200E+02	4.787E+00	-9.917E-02	5.383E+00	1.115E-01
93CA	"NO2"	19.00	6.377E-01	3.000E+01	3.401E+00	-2.417E-02	5.333E+00	3.790E-02
93CA	"NO2"	9.50	3.189E-01	6.316E+00	1.843E+00	-4.430E-03	5.780E+00	1.389E-02
94AB	"NO"	26.50	3.854E-01	1.067E+00	6.454E-02	-2.778E-04	1.674E-01	7.207E-04
94AB	"NO"	19.00	2.763E-01	1.067E+00	6.454E-02	-2.778E-04	2.335E-01	1.005E-03
94AB	"NO"	9.50	1.382E-01	1.067E+00	6.454E-02	-2.778E-04	4.671E-01	2.010E-03
94AB	"NO2"	26.50	3.854E-01	7.667E+00	2.037E+00	-2.899E-02	5.285E+00	7.520E-02
94AB	"NO2"	19.00	2.763E-01	3.286E+00	1.190E+00	-9.938E-03	4.305E+00	3.596E-02
94AB	"NO2"	9.50	1.382E-01	1.917E+00	6.506E-01	-3.986E-03	4.709E+00	2.884E-02

Table VII-7. (Cont.)

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
94BA	"NO"	26.50	3.854E-01	2.200E+00	7.885E-01	-2.182E-03	2.046E+00	5.661E-03
94BA	"NO"	19.00	2.763E-01	1.964E+00	6.751E-01	-1.753E-03	2.443E+00	6.344E-03
94BA	"NO"	9.50	1.382E-01	1.571E+00	4.520E-01	-1.039E-03	3.271E+00	7.519E-03
94BA	"NO2"	26.50	3.854E-01	6.000E+00	1.792E+00	-9.259E-03	4.649E+00	2.402E-02
94BA	"NO2"	19.00	2.763E-01	3.600E+00	1.281E+00	-4.815E-03	4.635E+00	1.742E-02
94BA	"NO2"	9.50	1.382E-01	1.929E+00	6.568E-01	-1.720E-03	4.753E+00	1.246E-02
94CA	"NO"	26.50	3.854E-01	3.000E+00	1.099E+00	-1.905E-03	2.850E+00	4.942E-03
94CA	"NO"	19.00	2.763E-01	2.800E+00	1.030E+00	-1.714E-03	3.726E+00	6.203E-03
94CA	"NO"	9.50	1.382E-01	1.909E+00	6.466E-01	-8.658E-04	4.680E+00	6.266E-03
94CA	"NO2"	26.50	3.854E-01	3.667E+00	1.299E+00	-2.424E-03	3.371E+00	6.290E-03
94CA	"NO2"	19.00	2.763E-01	2.340E+00	8.503E-01	-1.219E-03	3.077E+00	4.410E-03
94CA	"NO2"	9.50	1.382E-01	1.746E+00	5.573E-01	-6.782E-04	4.034E+00	4.908E-03
95AB	"NO"	26.50	2.628E-01	1.333E+00	2.877E-01	-1.852E-03	1.095E+00	7.047E-03
95AB	"NO"	19.00	1.884E-01	1.286E+00	2.513E-01	-1.587E-03	1.334E+00	8.424E-03
95AB	"NO"	9.50	9.421E-02	1.200E+00	1.823E-01	-1.111E-03	1.935E+00	1.179E-02
95AB	"NO2"	26.50	2.628E-01	2.222E+00	7.985E-01	-4.074E-03	3.039E+00	1.550E-02
95AB	"NO2"	19.00	1.884E-01	1.622E+00	4.834E-01	-2.072E-03	2.566E+00	1.100E-02
95AB	"NO2"	9.50	9.421E-02	1.364E+00	3.102E-01	-1.212E-03	3.292E+00	1.287E-02
95BA	"NO"	26.50	2.628E-01	1.964E+00	6.751E-01	-1.753E-03	2.569E+00	6.672E-03
95BA	"NO"	19.00	1.884E-01	1.833E+00	6.061E-01	-1.515E-03	3.217E+00	8.042E-03
95BA	"NO"	9.50	9.421E-02	1.375E+00	3.185E-01	-6.818E-04	3.380E+00	7.237E-03
95BA	"NO2"	26.50	2.628E-01	2.632E+00	9.676E-01	-3.263E-03	3.682E+00	1.242E-02
95BA	"NO2"	19.00	1.884E-01	1.786E+00	5.798E-01	-1.571E-03	3.077E+00	8.340E-03
95BA	"NO2"	9.50	9.421E-02	1.389E+00	3.285E-01	-7.778E-04	3.487E+00	8.256E-03
95CA	"NO"	26.50	2.628E-01	2.375E+00	8.650E-01	-1.447E-03	3.292E+00	5.508E-03
95CA	"NO"	19.00	1.884E-01	2.000E+00	6.931E-01	-1.053E-03	3.679E+00	5.587E-03
95CA	"NO"	9.50	9.421E-02	1.484E+00	3.950E-01	-5.099E-04	4.193E+00	5.412E-03
95CA	"NO2"	26.50	2.628E-01	2.935E+00	1.077E+00	-2.127E-03	4.098E+00	8.094E-03
95CA	"NO2"	19.00	1.884E-01	2.167E+00	7.732E-01	-1.282E-03	4.104E+00	6.804E-03
95CA	"NO2"	9.50	9.421E-02	1.596E+00	4.678E-01	-6.555E-04	4.966E+00	6.958E-03

Table VII-7. (Cont.)

RUN	GAS	HEIGHT	AHG-1	PO/PX	LN(PO/PX)	1/PO-1/PX	K1	K2
96AA	"NO"	26.50	1.542E+00	1.933E+00	6.592E-01	-3.218E-03	4.276E-01	2.088E-03
96AA	"NO"	19.00	1.105E+00	2.636E+00	9.694E-01	-5.643E-03	8.770E-01	5.105E-03
96AA	"NO"	9.50	5.527E-01	2.071E+00	7.282E-01	-3.695E-03	1.318E+00	6.685E-03
96AA	"NO2"	26.50	1.542E+00	2.400E+07	1.699E+01	-1.000E+05	1.102E+01	6.486E+04
96AA	"NO2"	19.00	1.105E+00	4.800E+00	1.569E+00	-1.583E-02	1.419E+00	1.432E-02
96AA	"NO2"	9.50	5.527E-01	2.000E+00	6.931E-01	-4.167E-03	1.254E+00	7.539E-03
96BA	"NO"	26.50	1.542E+00	3.143E+00	1.145E+00	-3.896E-03	7.428E-01	2.527E-03
96BA	"NO"	19.00	1.105E+00	2.444E+00	8.938E-01	-2.626E-03	8.086E-01	2.376E-03
96BA	"NO"	9.50	5.527E-01	2.444E+00	8.938E-01	-2.626E-03	1.617E+00	4.752E-03
96BA	"NO2"	26.50	1.542E+00	1.486E+01	2.698E+00	-2.665E-02	1.750E+00	1.728E-02
96BA	"NO2"	19.00	1.105E+00	2.600E+01	3.258E+00	-4.808E-02	2.948E+00	4.349E-02
96BA	"NO2"	9.50	5.527E-01	1.368E+00	3.137E-01	-7.085E-04	5.675E-01	1.282E-03
96CA	"NO"	26.50	1.542E+00	5.000E+00	1.609E+00	-4.000E-03	1.044E+00	2.595E-03
96CA	"NO"	19.00	1.105E+00	4.444E+00	1.492E+00	-3.444E-03	1.349E+00	3.116E-03
96CA	"NO"	9.50	5.527E-01	2.857E+00	1.050E+00	-1.857E-03	1.899E+00	3.360E-03
96CA	"NO2"	26.50	1.542E+00	9.000E+01	4.500E+00	-9.889E-02	2.919E+00	6.414E-02
96CA	"NO2"	19.00	1.105E+00	1.000E+01	2.303E+00	-1.000E-02	2.083E+00	9.047E-03
96CA	"NO2"	9.50	5.527E-01	4.286E+00	1.455E+00	-3.651E-03	2.633E+00	6.606E-03
97AA	"NO"	26.50	4.720E-01	2.250E+00	8.109E-01	-5.556E-03	1.718E+00	1.177E-02
97AA	"NO"	19.00	3.384E-01	2.250E+00	8.109E-01	-5.556E-03	2.397E+00	1.642E-02
97AA	"NO"	9.50	1.692E-01	1.800E+00	5.878E-01	-3.556E-03	3.474E+00	2.102E-02
97AA	"NO2"	26.50	4.720E-01	1.600E+00	4.700E-01	-2.143E-03	9.959E-01	4.540E-03
97AA	"NO2"	19.00	3.384E-01	1.436E+00	3.618E-01	-1.557E-03	1.069E+00	4.601E-03
97AA	"NO2"	9.50	1.692E-01	1.273E+00	2.412E-01	-9.740E-04	1.425E+00	5.757E-03
97BA	"NO"	26.50	4.720E-01	2.273E+00	8.210E-01	-2.545E-03	1.740E+00	5.393E-03
97BA	"NO"	19.00	3.384E-01	2.000E+00	6.931E-01	-2.000E-03	2.048E+00	5.911E-03
97BA	"NO"	9.50	1.692E-01	1.429E+00	3.567E-01	-8.571E-04	2.108E+00	5.066E-03
97BA	"NO2"	26.50	4.720E-01	3.226E+00	1.171E+00	-4.452E-03	2.482E+00	9.432E-03
97BA	"NO2"	19.00	3.384E-01	2.222E+00	7.985E-01	-2.444E-03	2.360E+00	7.224E-03
97BA	"NO2"	9.50	1.692E-01	1.695E+00	5.276E-01	-1.390E-03	3.119E+00	8.215E-03

Table VII-7. (Cont.)

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RUN     GAS      HEIGHT    AHG-1        PO/PX        LN(PO/PX)    1/PO-1/PX     K1           K2

97CA    "NO"     26.50     4.720E-01    4.955E+00    1.600E+00    -3.628E-03    3.391E+00    7.687E-03
97CA    "NO"     19.00     3.384E-01    3.825E+00    1.341E+00    -2.591E-03    3.964E+00    7.658E-03
97CA    "NO"      9.50     1.692E-01    2.180E+00    7.793E-01    -1.083E-03    4.606E+00    6.399E-03

97CA    "NO2"    26.50     4.720E-01    2.847E+00    1.046E+00    -1.802E-03    2.217E+00    3.819E-03
97CA    "NO2"    19.00     3.384E-01    2.050E+00    7.178E-01    -1.024E-03    2.121E+00    3.027E-03
97CA    "NO2"     9.50     1.692E-01    1.737E+00    5.523E-01    -7.193E-04    3.265E+00    4.251E-03


ERROR IN STATEMENT 11.21:  END OF FILE ON INPUT
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Table VII-8. Rate Constants from the OAP Data[10]

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DO PART 15
   OUP = 'GAROUT

RUN     GAS      HEIGHT     AHG-1        PO/PX       LN(PO/PX)     1/PO-1/PX       K1           K2

14-1    "NO"      1.50    1.243E-01    1.268E+00    2.376E-01    -9.822E-04    1.912E+00    7.905E-03
14-1    "NO2"     1.50    1.243E-01    1.243E+00    2.177E-01    -9.347E-04    1.752E+00    7.523E-03
14-2    "NO"      1.50    1.243E-01    1.380E+00    3.220E-01    -1.026E-03    2.592E+00    8.259E-03
14-2    "NO2"     1.50    1.243E-01    1.351E+00    3.009E-01    -9.892E-04    2.422E+00    7.962E-03
14-3    "NO"      1.50    1.243E-01    1.439E+00    3.637E-01    -9.232E-04    2.927E+00    7.430E-03
14-3    "NO2"     1.50    1.243E-01    1.409E+00    3.428E-01    -9.087E-04    2.759E+00    7.314E-03
14-4    "NO"      1.50    1.243E-01    1.561E+00    4.452E-01    -9.756E-04    3.583E+00    7.851E-03
14-4    "NO2"     1.50    1.243E-01    1.563E+00    4.463E-01    -1.023E-03    3.592E+00    8.230E-03
14-5    "NO"      1.50    1.243E-01    1.602E+00    4.716E-01    -8.664E-04    3.795E+00    6.973E-03
14-5    "NO2"     1.50    1.243E-01    1.578E+00    4.561E-01    -8.742E-04    3.670E+00    7.035E-03
14-6    "NO"      1.50    1.243E-01    1.469E+00    3.842E-01    -5.765E-04    3.092E+00    4.640E-03
14-6    "NO2"     1.50    1.243E-01    1.913E+00    6.486E-01    -1.151E-03    5.220E+00    9.265E-03
15-1    "NO"      1.50    1.243E-01    1.254E+00    2.264E-01    -9.937E-04    1.822E+00    7.998E-03
15-1    "NO2"     1.50    1.243E-01    1.239E+00    2.146E-01    -9.361E-04    1.727E+00    7.534E-03
15-2    "NO"      1.50    1.243E-01    1.330E+00    2.850E-01    -9.613E-04    2.294E+00    7.737E-03
15-2    "NO2"     1.50    1.243E-01    1.350E+00    2.999E-01    -9.974E-04    2.413E+00    8.027E-03
15-3    "NO"      1.50    1.243E-01    1.361E+00    3.084E-01    -8.009E-04    2.482E+00    6.446E-03
15-3    "NO2"     1.50    1.243E-01    1.395E+00    3.327E-01    -8.741E-04    2.677E+00    7.035E-03
15-4    "NO"      1.50    1.243E-01    1.412E+00    3.451E-01    -7.422E-04    2.777E+00    5.973E-03
15-4    "NO2"     1.50    1.243E-01    1.445E+00    3.682E-01    -8.009E-04    2.964E+00    6.445E-03
15-5    "NO"      1.50    1.243E-01    1.433E+00    3.595E-01    -6.518E-04    2.893E+00    5.246E-03
15-5    "NO2"     1.50    1.243E-01    1.465E+00    3.822E-01    -7.005E-04    3.076E+00    5.638E-03
15-6    "NO"      1.50    1.243E-01    1.476E+00    3.891E-01    -6.186E-04    3.131E+00    4.979E-03
15-6    "NO2"     1.50    1.243E-01    1.511E+00    4.125E-01    -6.384E-04    3.320E+00    5.138E-03
17-1    "NO"      1.50    1.243E-01    1.351E+00    3.005E-01    -1.388E-03    2.419E+00    1.117E-02
17-1    "NO2"     1.50    1.243E-01    1.514E+00    4.149E-01    -2.035E-03    3.339E+00    1.638E-02
17-2    "NO"      1.50    1.243E-01    1.379E+00    3.215E-01    -1.035E-03    2.588E+00    8.330E-03
17-2    "NO2"     1.50    1.243E-01    1.516E+00    4.161E-01    -1.482E-03    3.349E+00    1.193E-02
17-3    "NO"      1.50    1.243E-01    1.396E+00    3.334E-01    -8.563E-04    2.683E+00    6.891E-03
17-3    "NO2"     1.50    1.243E-01    1.580E+00    4.576E-01    -1.330E-03    3.683E+00    1.071E-02
17-4    "NO"      1.50    1.243E-01    1.477E+00    3.900E-01    -7.973E-04    3.138E+00    6.417E-03
17-4    "NO2"     1.50    1.243E-01    1.653E-00    5.027E-01    -1.163E-03    4.046E+00    9.359E-03
17-5    "NO"      1.50    1.243E-01    1.528E+00    4.238E-01    -7.749E-04    3.411E+00    6.237E-03
17-5    "NO2"     1.50    1.243E-01    1.652E+00    5.022E-01    -9.817E-04    4.042E+00    7.901E-03
17-6    "NO"      1.50    1.243E-01    1.561E+00    4.455E-01    -7.402E-04    3.586E+00    5.957E-03
17-6    "NO2"     1.50    1.243E-01    1.684E+00    5.211E-01    -8.883E-04    4.194E+00    7.149E-03
18-1    "NO"      1.50    1.243E-01    1.277E+00    2.442E-01    -1.091E-03    1.965E+00    8.783E-03
18-1    "NO2"     1.50    1.243E-01    1.202E+00    1.839E-01    -8.102E-04    1.480E+00    6.521E-03
18-2    "NO"      1.50    1.243E-01    1.326E+00    2.822E-01    -9.455E-04    2.272E+00    7.610E-03
18-2    "NO2"     1.50    1.243E-01    1.363E+00    3.098E-01    -1.067E-03    2.493E+00    8.584E-03
18-3    "NO"      1.50    1.243E-01    1.342E+00    2.943E-01    -7.613E-04    2.369E+00    6.127E-03
18-3    "NO2"     1.50    1.243E-01    1.318E+00    2.759E-01    -7.135E-04    2.221E+00    5.743E-03
18-4    "NO"      1.50    1.243E-01    1.381E+00    3.226E-01    -6.893E-04    2.596E+00    5.547E-03
18-4    "NO2"     1.50    1.243E-01    1.413E+00    3.461E-01    -7.477E-04    2.785E+00    6.018E-03
18-5    "NO"      1.50    1.243E-01    1.453E+00    3.738E-01    -6.962E-04    3.009E+00    5.603E-03
18-5    "NO2"     1.50    1.243E-01    1.429E+00    3.571E-01    -6.582E-04    2.874E+00    5.297E-03
18-6    "NO"      1.50    1.243E-01    1.472E+00    3.867E-01    -6.140E-04    3.112E+00    4.942E-03
18-6    "NO2"     1.50    1.243E-01    1.485E+00    3.953E-01    -6.168E-04    3.182E+00    4.964E-03

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APPENDIX VIII. LABORATORY STRIPPER TESTS

Table VIII-1

Run	Date	Page	L (cc/min)	G (cc/min at STP)	Gas	% H_2SO_4 In	% H_2SO_4 Out	% $HNSO_5$ In	% $HNSO_5$ Out	% Stripping	% NO_2	% NO	Column Temp (°F)	Acid Temp (°F)	Packing	Dryer	Comments
1	27 July	60	4.5	100	N_2	80	80	1.0	1.0	0	0.0	0.0	RT	RT	Saddles	Cold Trap	Runs 1-6 of doubtful validity were, therefore, repeated as Runs 13-17
2		61	5.4	250			—		0.9	10	0.0	0.0	RT				—
3			4.6	100			—		0.9	10	0.3	0.0	170				—
4		↓	4.2	250			—		0.9	10	0.4	0.0	170				—
5		62	3.7	100			—		0.6	40	0.7*	~5.0	300				*NO_2 fluctuating probably due to top of column being cold
6	↓	62	3.7	250	↓		—	↓	0.3	70	0.7	~3.2	280			↓	—
7	28 July	64	4.3	100	Air		—	0.9	0.9	0	0.0	0.0	RT			Sieves	—
8			4.9	250			—			0	0.0	0.0	RT				—
9		↓	4.5	100			—			0	0.3	0.0	172				—
10		65	4.3	250			—		↓	0	0.3	0.0	174				—
11			4.3	250			†		0.07	90	~2*	0.0	270				*NO_2 fluctuating probably due to top of column being cold †S.G. = 1.742 at 82°F
12	↓	↓	4.1	250	↓	↓	*		0.17	80	~1.2	0.0	271			↓	*S.G. = 1.735 at 84°F
13	29 July	67	4.9	100	N_2	82	82		0.9	0	0.0	0.0	RT			Cold Trap	—
14			4.8	250					0.9	0	0.0	0.0	RT				—
15			4.1	100						0	0.2	0.0	185				—
16			5.5	250				↓		0	0.3	0.1	182				—
17	↓	↓	5.0	250	↓				0.5	45	~1	0.6	280	↓	↓		—
18	30 July	69	—	—	—			0.82	—	—	—	—	—	—	Carbon	↓	Column blocked with fines. Wash with 80% H_2SO_4
19	2 Aug	71	8.3	100	N_2			0.74	0.42	43	0.0	0.0	RT	RT		Sieves	Heat sample lines at outlet but not at top of column
20	2 Aug	71	5.1	250	N_2	↓	↓	0.74	0.60	19	0.0	1-2	RT	RT	↓	Sieves	NO_2 jumps up to ~1% every time a sample is taken even though no air enters the system

192

Table VIII-1. (Continued)

Run	Date	Page	L (cc/min)	G (cc/min at STP)	Gas	% H_2SO_4		% $HNSO_5$		% Stripping	% NO_2	% NO	Column Temp (°F)	Acid Column (°F)	Packing	Dryer	Comments
						In	Out	In	Out								
21	2 Aug	71	5.0	100	N_2	82	82	0.74	0.03	96	0.0	>5	173	RT	Carbon	Sieves	—
22			4.0	250					0.02	97	0.0	>5	172				—
23			3.9	100					0.02	97	0.0	>5	320				—
24			4.9	250					0.02	97	0.0	>5	317				—
25		72	~4	100	Air	—	—	—	—	—	0.2	0.0	320				Air run for only 15 min NO_2 climbing
26	3 Aug	74	8.0	100		79	79	0.92	0.85	8	0.3	0.0	RT			Cold Trap	—
27			6.1	250					0.86	7	0.2	0.1	RT				—
28			6.5	100					0.94	0	0.3	0.0	181				—
29			6.6				81		0.03	97	2-14	>5	338				—
30			6.6				79	2.1	0.13	94	~2	>5	326				—
31	4 Aug	77	5.7				80	2.1	0.03	99	0.4	>5	280				—
32		83	3.3				—	0.85	0.02	98	0.4	>5	271				—
33		83	3.3				—	0.85			~10	0.2	271				High NO_2 occurred on flooded column. Returned to lower NO_2 when column stopped flooding
34		77	3.3	200			—				0.7	0.7	265				—
35			2.7		N_2		—				<0.4	>5	262				—
36			2.8		N_2		—				0.0	>5	287				—
37	5 Aug	84	2.9		Air	80	—	0.86	0.09	90	1.2	0.0	280	280			—
38		85	2.9		N_2		—	0.90	<0.01	100	0.1	>5	190	185			—
39		85	2.6				—				0.0	>5	237	246			—
40		87	3.2				—				0.0	>5	270	268			—
41		87	2.6				—				0.0	>5	313	317			—
42	6 Aug	88	2.8		Air		—	0.83	0.08	90	1 to 6	0.0	190	185			—
43		88	2.3				—		0.04	95	~1	0.0	226	230			—
44		89	2.8				—		<0.01	100	1.8	0.0	277	256			—
45		91	4.1				—		<0.01	100	1.6	0.0	304	296			As temp rose from 280 to 304 NO_2 rose to about 8% and then decreased to 1.6% within an hour
46		91	4.7				—	0.01	0.0	—	0.0	0.0	312	270			—

Table VIII-2

No.	Feed Acid Concentration (% $HNSO_5$)*	Air Feed Rate (cc/min)	NO_x in Effluent (%)		Percent Denitration	Material Balance Error (%)†
			NO_2	NO		
1	0.59	800	1.50	0.11	99.0	16.5
2	0.59	800	1.52	0.11	99.3	25.7
3	0.59	800	1.20	0.10	**	41.2
4	0.68	800	3.20	0.09	99.0	-35.4
5	0.83	800	3.52	0.17	98.9	2.8
6	0.73	800	1.30	0.63	**	35.1
7	0.59	400	1.06	0.04	**	76.0
8	0.83	400	2.16	0.29	71.1	37.9
9	0.83	400	2.96	0.27	99.0	56.5
10	0.83	400	3.76	0.16	**	41.0
11	0.83	400	3.36	0.19	**	53.9

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* Acid fed at 10 cc/min.

** ~99% denitrated.

† Material balance error = $\frac{NO_x \text{ (in)} - NO_x \text{ (out)}}{NO_x \text{ (in)}}$

APPENDIX IX. INSTRUMENTATION CALIBRATION

A. Calibration of the UV Spectrophotometer for NO_2 at Concentrations Above 1%

During most of the early experimentation, the UV analyzer has been used for the analysis of NO_2 at concentrations up to 1% NO_2. During some of the stripper experimentation (Section VIII of this report), the UV analyzer was used in cases where the expected NO_2 concentrations were as high as 10%. To allow us to use the UV spectrometer in this NO_2 concentration range, we have checked the response curve by preparing known gas samples. The dependence of the response curve on flow rate, cell temperature (i.e., span setting), and diluent gas was determined.

The gas samples were prepared by mixing (at constant flow rate) NO, O_2, and Ar or N_2 in the NO_x reactor, allowing sufficient time for greater than 98% conversion to NO_2. The residual NO concentration was determined and corrected for. Using properly calibrated flow meters, it was possible to prepare gas mixtures containing up to 15% NO_2. The UV spectrometer gain was set at one concentration, with a known gas sample standard mixture from Matheson. Then the higher concentration samples we prepared were passed through the UV and IR cells, and a UV spectrometer calibration curve was constructed. The spectrometer response was found to be sensitive to cell temperature (span setting) flow rates but independent of the diluent gas (N_2 or Ar), as expected. Three typical response curves are shown in Fig. IX-1.

The unusual shape of the response curves indicates that a linear extrapolation from low concentrations will give inappropriate analyses. The dual-valued curves make it difficult to determine which of two possible concentrations might be indicated by any given recorder response (e.g., 150). Representatives of duPont indicate that these problems can be most readily overcome by using a shorter analysis cell. Up to this time a 15-in. cell had been used. A new 1.5-in. cell was installed in the spectrometer to overcome the problem.

The change in shape of the response curves, as slow rate and cell temperature are varied, deserves special attention. It verifies the importance of heated sample lines, a thermostatted sample warmer by the UV analyzer, and standard flow rates. This was used, in both laboratory and miniplant experimentation.

B. IR Spectrometer Calibration

The IR spectrometer gain was first adjusted with a known gas mixture from Matheson.

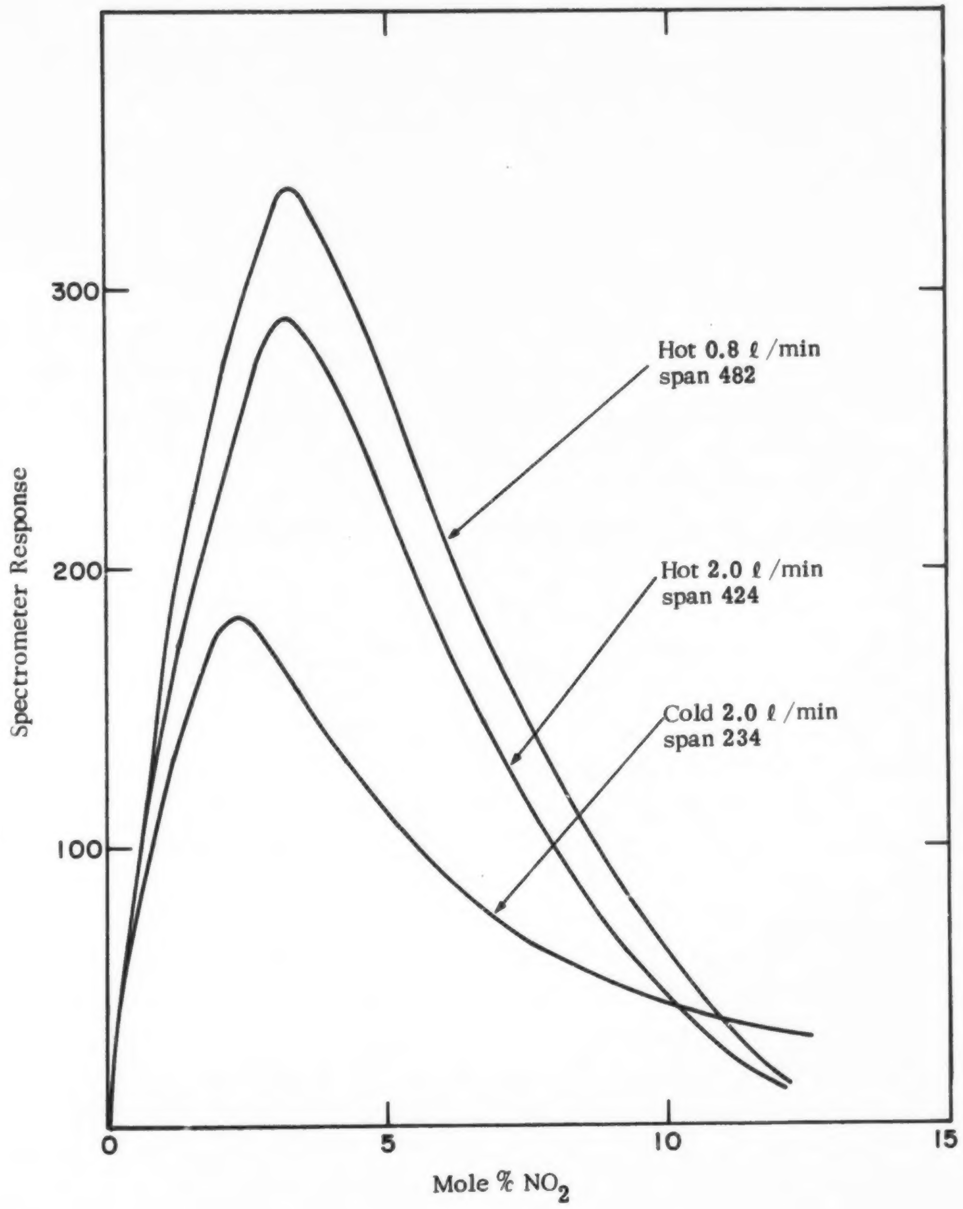

Fig. IX-1. UV spectrometer calibration curve for NO_2 with the 15-in. cell.

196

The IR cell was calibrated for high NO concentrations (0 to 100%) by feeding known mixtures of NO and Ar to the IR cell. The calibration curve is mildly dependent on flow rate. A typical calibration curve is given in Fig. IX-2. The basic conclusion one may draw is that accurate analysis for NO above the 1% level requires very careful standardization techniques, and such measurements should be avoided, if possible.

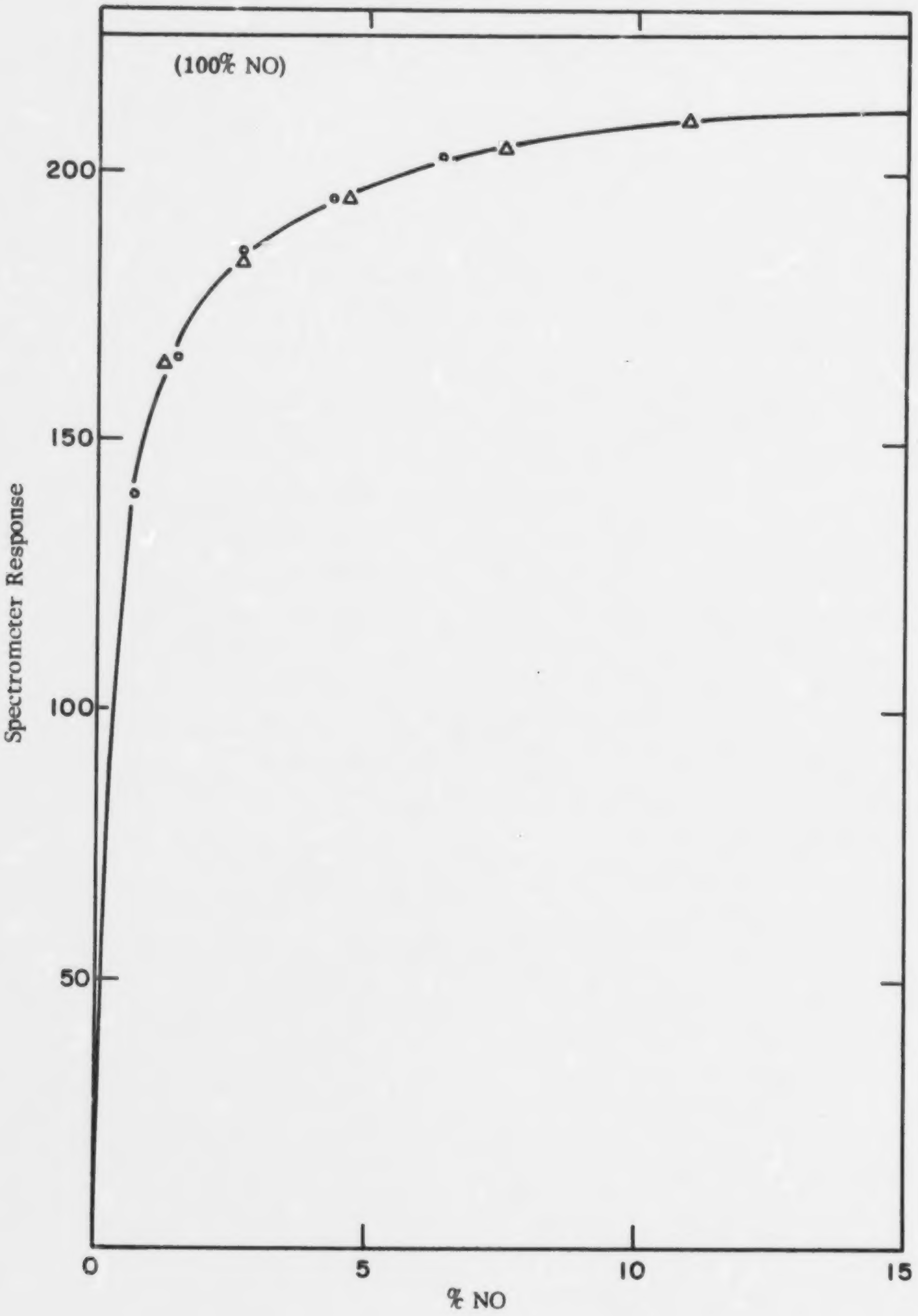

Fig. IX-2. IR spectrometer calibration curve for NO.

APPENDIX X. OXIDATION OF NO TO NO_2 FOR MINIPLANT GAS FEED

Miniplant experimentation requires a source of NO_2 for the oxidation of SO_2. Sufficient NO_2 is required to form 6000 ppm NO_2 at 12 SCFM. It is preferable to have an easily regulated NO_x supply with less than 10% of the NO_x present as NO. Higher fractions of NO place an undue loading on the scrubber and the stripper.

Of the three possible sources of NO_x:

1. Commercial NO_2,
2. Homogeneous oxidation of NO, and
3. Catalytic oxidation of NO,

we conclude that the most expedient and satisfactory source is homogeneous oxidation of NO. Use of commercially available NO_2 involves additional handling and control problems which may be avoided using NO as a source. Catalytic oxidation of NO with air and activated charcoal (dry) has been shown to involve the potential dangers of thermal runaway at high NO concentrations, e.g., temperature changes of +4 °F/sec have been observed with 11.6% NO in air.

Homogeneous oxidation of NO with O_2 was studied using Ar and N_2 as diluent gases. The gases were obtained in high pressure cylinders from Matheson and Airco. In-house compressed air was used without drying. The reactor, a 4 ft. length of 4-in. glass pipe, was held at an ambient temperature of about 70 °F. Gas sampling lines leading to the UV and IR cells were 3/16-in. I.D. Teflon lines with a total length of about 30 ft. The flow rate from the reactor, through the UV cell up to the IR cell, was 2 ft^3/min. The residence time in the sample lines was about 0.2 sec. Residence time in the UV cell was less than 1 sec. One may thus ignore sampling line-residence times in kinetic calculations. Experimental results are presented in Fig. X-1.

To allow for the performance of a sufficient number of experiments in a reasonable time, we must pay careful attention to possible sources of analytical errors. In the present case, we must consider the results obtainable with the UV and IR analyzers. As discussed in Appendix IX, concentrations above 2% (as measured by either analyzer) may be expected to give only semiquantitative information about the gas being analyzed. At concentrations between 500 ppm and 1%, low baseline drift and frequent calibrations yield data accurate to ± 2% of the indicated value. We can most accurately evaluate rate constants by using data corresponding to the 500 ppm in 1% regions and in concentration regions where the kinetic equations are not

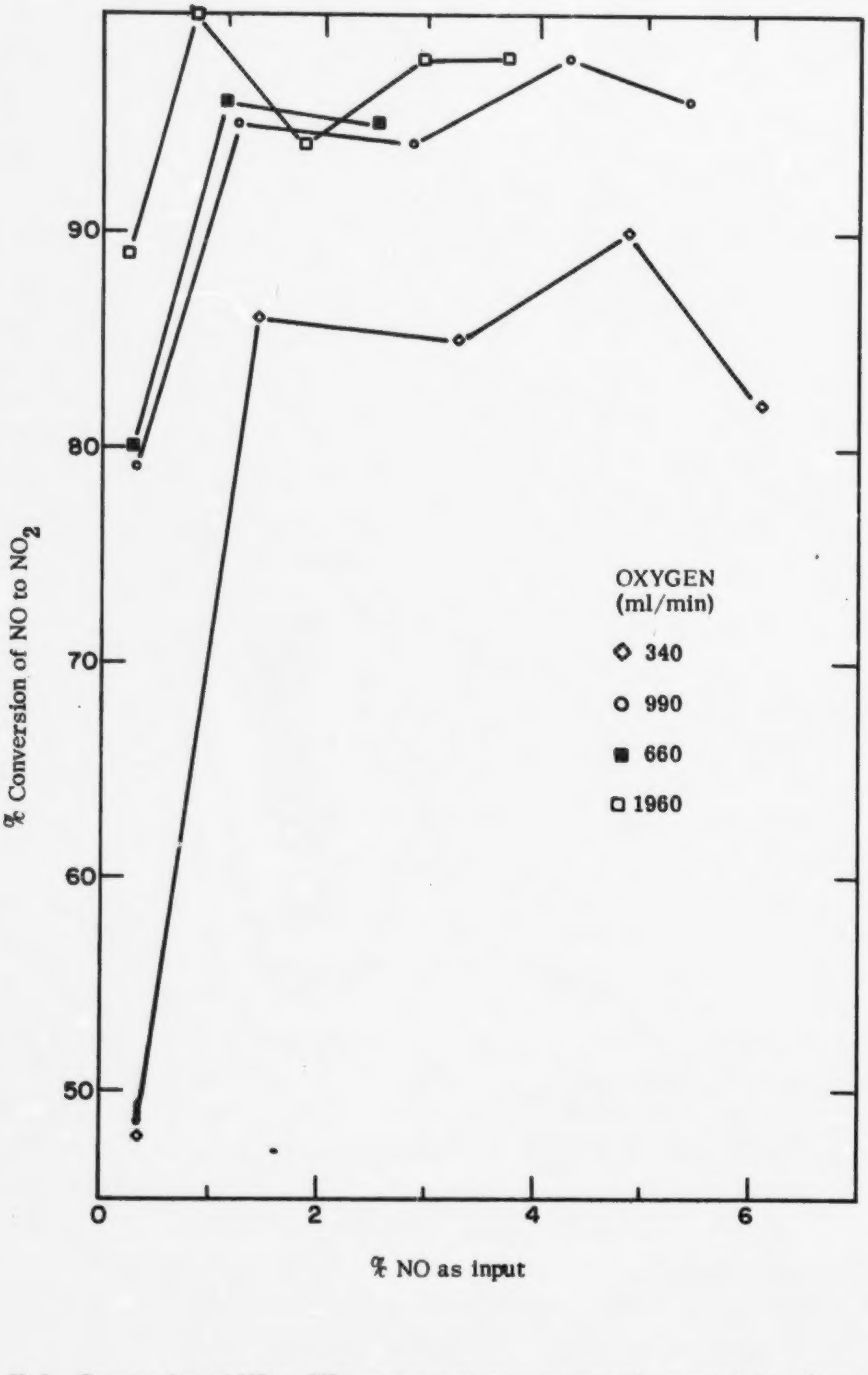

Fig. X-1. Conversion of NO to NO$_2$ at room temperature without a catalyst (argon flow was 1740 ml/min).

200

sensitive to small analytical errors (10 to 90% conversion of NO to NO_2). These requirements are met by the starred data in Fig. X-1, and the rate constants so obtained may be used to calculate results which would otherwise require excessive experimentation.

The reaction $2NO + O_2 = 2NO_2$ is expected to obey third-order kinetics, and this has been verified by M. Bodenstein [Z. Elektrochem 22, 327 (1916) and Z. Physik. Chem., 100, 68 (1922)]. If we denote the initial O_2 partial pressure by a (atm), the initial NO partial pressure by b (atm), the instantaneous partial pressure of NO_2 by x (atm), and time by t (sec), the rate of formation of NO_2 is then given by:

$$\frac{dx}{dt} = K \left(a - \frac{x}{2}\right) (b - x)^2$$

The integrated form is:

$$\frac{2a}{b} - \frac{2a-x}{b-x} + \ln\left[\frac{2a-x}{b-x} \quad \frac{b}{2a}\right] = -\frac{1}{2} (2a-b)^2 Kt$$

or the equivalent form

$$\frac{1}{b} - \frac{1}{b-x} + \frac{1}{2a-b} \ln\left[\frac{2a-x}{b-x} \quad \frac{b}{2a}\right] = -\frac{Kt}{2} .$$

Given a value for a, b, x, and t, one may solve for the rate constant K. In our case, the values were:

$a = 0.169$ atm O_2
$b = 0.030$ atm NO
$x = 0.86$ b
$t = 44.1$ sec

which leads to

$$K = 29.3 \text{ atm}^{-2}\text{sec}^{-1} .$$

Now that we have solved for K, it is possible to predict the residence time required for any degree of conversion of NO to NO_2 and starting with any desired initial O_2 and NO partial pressures.

We know from experimental data of Fig. X-1 that it is possible to achieve 95% or greater conversion of NO to NO_2 at high O_2 concentrations. It is of interest to know what might happen if air were used with NO at varying residence times. This is easily calculated. In Table X-1, we present the time necessary to reach the specified conversion of NO to NO_2 starting with various NO partial pressures.

The information which is of more direct use to us concerns the number of linear feet required to generate sufficient NO_2 for 6000 ppm of usable NO_2 in a 12 SCFM gas stream. At 99% conversion of NO to NO_2, one obtains 98% usable NO_2, and to get 6000 ppm usable NO_2, one needs:

Table X-1. Conversion of NO to NO_2 with Air (See Text)

Starting NO (%)	Time to Specified Conversion (sec) 0.8	0.9	0.95	0.99
3	23.4	53.2	113.2	595
10	8.6	20.2	44.0	238
20	6.50	17.0	39.8	235
25	7.09	20.9	54.1	367
29	9.1	34.2	119.8	1532

$$\frac{12 \text{ SCFM} \pm 0.006}{0.98} = 0.0735 \text{ SCFM of NO.}$$

Similarly for 95, 90, and 80% conversion, one requires 0.80, 0.90, and 0.120 SCFM of NO, respectively.

To calculate F, the required number of cubic feet of NO_x reactor volume, we use the formula:

$$F = \frac{T \cdot S}{60 \cdot F} \ .$$

Where T = the time in seconds to achieve the desired degree of conversion, S = the number of SCFM of NO feed required at the specified degree of conversion, 60 = the number of sec/min, and F = the fraction of gas entering the reactor which is NO. The number of linear feet of reactor required is F/0.0873. Using this formula, Table X-2 and Fig. X-2 were prepared.

Fig. X-2 vividly illustrates that greater than 95% conversior of NO to NO_2 conversion with air can be expected with 10 ft of piping as long as the portion of NO going into the NO_x reactor is between 10 and 29%. It also illustrates that, if the portion of NO going into the NO_x reactor is much less than 10%, drastically larger reactors are required to achieve high yields of NO_2.

Table X-2. Required Length of 4-in. NO_x Reactor to Oxidize NO to NO_2 with Air and Obtain 6000 ppm NO_2 in a 12 SCFM Stream by Dilution

Starting NO (%)	Length of Reactor for Specified Conversion (ft)			
	0.8	0.9	0.95	0.99
3	17.8	30.5	57.7	278
10	1.97	3.44	6.72	33.4
20	0.76	1.47	3.03	16.5
25	0.66	1.41	3.28	20.6
29	0.71	2.02	6.32	74.1

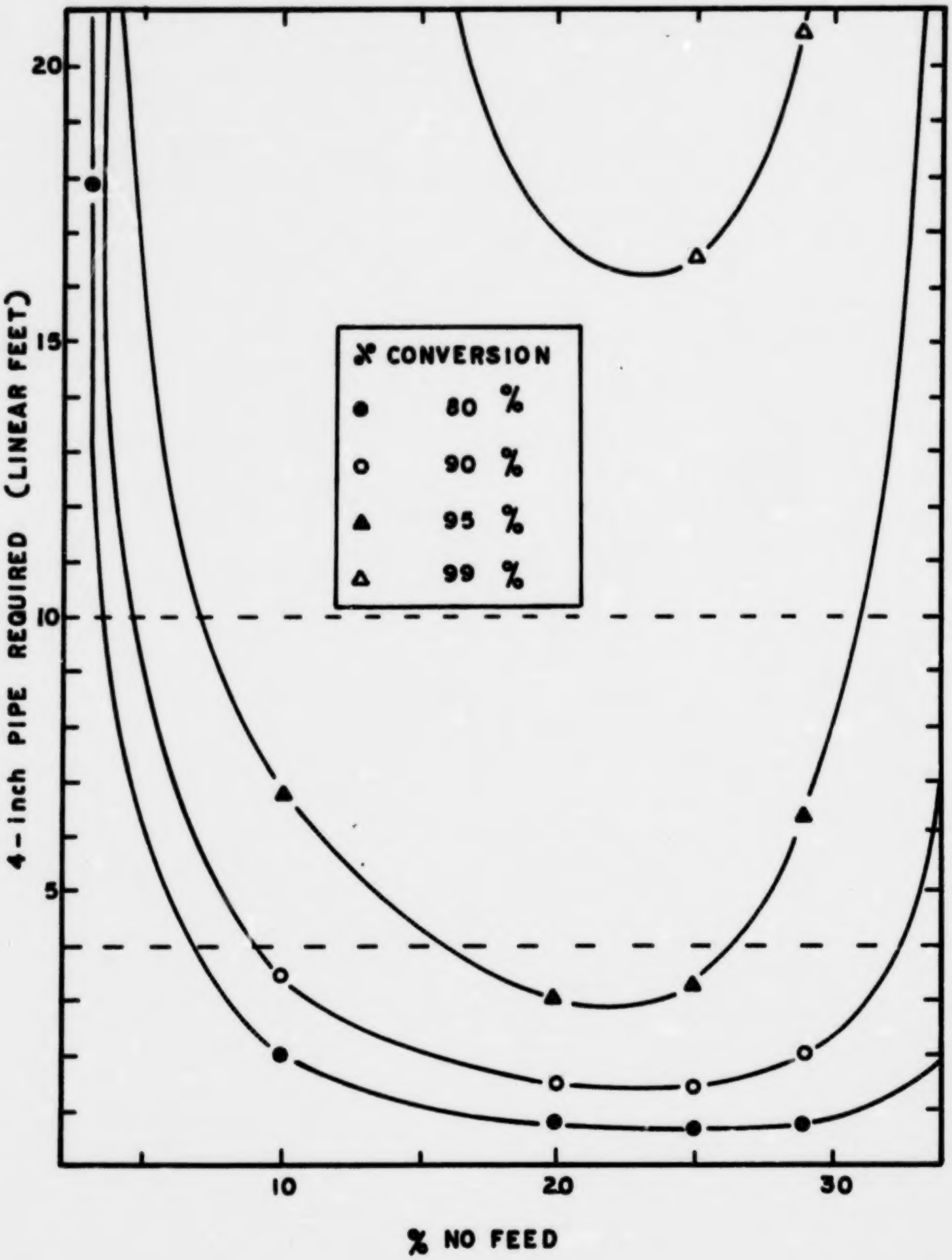

Fig. X-2. Conversion of NO to NO_2 at room temperature without catalyst (number of linear feet of 4-in. pipe required to give 6000 usable ppm NO_2 when diluted into a 12-SCFM stream; see text).

204